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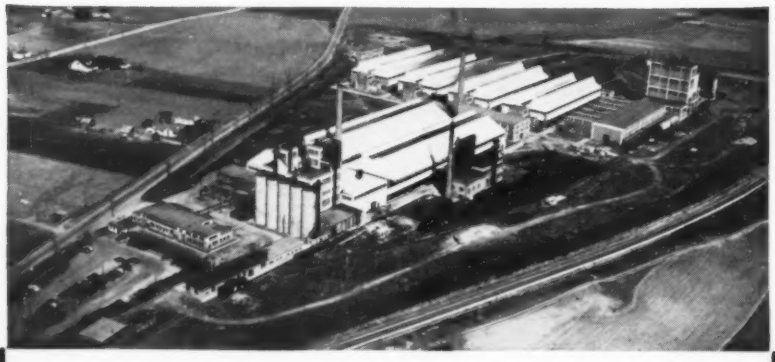

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How to Determine Impurities in Copper Plating Baths

SILVER in copper plating baths may be determined colorimetrically, by using a carbon tetrachloride solution of dithizone to produce the colored solution. The hue measured is that of the mixed color of silver keto dithizonate and cupric keto dithizonate. Small amounts of certain other metals do not interfere, nor is separation of the silver required.

CHLORIDE, also, may be determined colorimetrically. The method depends upon the addition of a known quantity of silver ions and determining the excess of silver ions remaining after silver chloride has been precipitated. The excess is determined by the mixed color of silver and cupric dithizonate.

LEAD traces are determined as follows: Organic material is oxidized with phosphoric acid and the lead is separated from interfering ions by extracting with a carbon tetrachloride solution of dithizone in the presence of potassium cyanide. Transmittance of the solution is measured and the quantity of lead determined from a calibration curve.

CHROMIUM: To determine chromate chromium, nitric acid is added to oxidize any reducing agents, phosphoric acid is added to make a complex with Fe^{+++}, and diphenylcarbazide is added to form a colored complex. Transmittancy of the solution is measured, and the amount of CrO_3 present as chromate is read off the calibration curve.

For total chromium analysis, iron is first removed by precipitation. The chromium is oxidized first by fuming with perchloric acid and then by boiling with ammonium persulfate in the presence of silver ions. The silver is precipitated. The solution is centrifuged, the transmittancy of the clear supernatant solution measured, and the amount of CrO_3 present is determined from the calibration curve.

NICKEL can be accurately determined colorimetrically by forming nickel dimethylglyoxime but copper must first be removed quantitatively.

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Editorial

To Keep Teachers Teaching

A SERIOUS PROBLEM confronting the universities and colleges, particularly those dependent upon private endowment, is the retention of their younger members of teaching staff. In these inflationary days the economic pressure upon the younger faculty members is such as to encourage their consideration of attractive opportunities in other fields. Particularly in science and engineering, industrial positions offer two or three thousand dollars a year more than academic institutions can pay for teaching positions requiring men of comparable ability. Industry places a high premium on exceptional talent and there is keen competition for those who will yield to temptation and forsake teaching careers. This depletion will lower the quality of teaching and inevitably the quality of the trained product. The seriousness of the situation is further aggravated by anticipated reductions in enrollment where tuition is a major source of income. State supported schools are faring a little better as is indicated by the fact that they have been able to entice distinguished young teachers from the faculties of the foremost old privately endowed universities. However, they too have the same problem if only in lesser degree.

The problem in simple terms is how to get the money necessary to supplement the present salaries of the teaching staff in the age group 25 to 35 years. It does not represent a large figure in these days. For example, it would require five million dollars on an annual basis to add a thousand dollars to the salaries of fifty individuals in a hundred institutions. This does not seem too large an investment to make in the maintenance of the intellectual resources of the country. Since provision of competent instruction at the college level is in the public interest, it could be argued that the necessary funds should come from taxation, that is, government support. While this may turn out to be necessary in the case of the humanities, it should not be so in science and engineering. While it is conceivable that some of the funds of the National Science Foundation should be diverted to the support of teachers rather than given to the taught in the form of fellowships, the principal source of these necessary supplemental funds should be from the industries that use the trained product.

American industry in recent years has made a generous contribution toward higher education in the establishment of hundreds of university fellowships. Rather than create more fellowships which would accentuate the problem, it is suggested that industrial concerns make liberal annual contributions to the universities for use in supplementing the salaries of their ablest young faculty members below the rank of professor. —RMB

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The Mechanism of Exchange Between Radioactive Ions in Solution and Metal Surfaces[1]

M. T. Simnad

Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

AND

R. C. Ruder

Pigments Division, E. I. du Pont de Nemours Company, Wilmington, Delaware

ABSTRACT

The mechanism of exchange between metals and ions in solution has been studied with radioactive cobalt ions in solutions into which various metals with different surface treatments were immersed in the presence and absence of oxygen. The metals were washed after various times of immersion in the solutions, their acquired radioactivities measured, and the distribution of radioactive cobalt on the surfaces shown by means of autoradiographs. The results indicate that local cell action, due to differences of potential on the metal surfaces, is the factor which governs the radioactivity acquired by the metals. By applying Faraday's law, it has been possible to calculate the magnitudes of local cell currents on the metal surfaces from the acquired activities.

Introduction

The exchange between a metal and ions in solution has received very little attention despite its great importance to the understanding of the behavior of metals in solutions. With the advent of radioactive isotopes, studies of this phenomenon can be made in a way that was not possible with the methods available hitherto. The first experimental evidence of such exchange was presented by Hevesy (1) when he showed that metallic lead exchanges with thorium B ions in solution. The amount of the exchange corresponded to a depth of about 1000 atom layers, in the lead, and he concluded that the lead atoms from the interior of the metal diffuse to the surface and take part in the exchange. This explanation is difficult to accept in view of the short time and low temperature involved in these experiments.

In 1940 Rollin (2) extended the work of Hevesy by using radioactive silver in solution and measuring the exchange on silver, gold, and platinum immersed in the solution. All three metals acquired an activity representing the transference of about 100 atom layers of silver from the solution. The activity was not reduced after washing with water for 48 hours. The only reasonable mechanism seemed to be that of local electrolysis caused by the existence of irregularities on the surface of the metals. It was a puzzling fact that gold and platinum, both more noble metals than silver, had acquired activities.

In 1948 Hensley *et al.* (3) reported the results of some experiments in which soft glass samples immersed in aqueous solutions containing radioactive sodium ions were found to have acquired up to five monolayers of sodium ions after two hours' immersion. They also claim that from 0.2 to 5 monolayers of sodium ions are sorbed by cleaned aluminum, steel, silver, and platinum during a few hours' immersion at room temperature. They interpret their results in terms of the sorption of the sodium ions upon these surfaces.

Recently, after this project on metal-ion exchange experiments had been started, Coffin and Tingley (4) published a note on the exchange of silver ions between aqueous solution and surfaces of metallic silver. They confirm Rollin's work on silver, and also find that mechanically polished and cold-worked silver acquires far greater activity than etched silver. They suggest that two exchange mechanisms are involved: (*a*) the electrochemical, accounting for most of the activity taken up by the crystalline areas, and (*b*) the kinetic, responsible for the activity taken up by the polished surfaces and the anodic areas of cold-worked specimens.[2]

None of these studies show evidence of the surface distribution of the active ions, nor do they draw conclusions from their results regarding the over-all magnitude of the local cell currents. In the present work, the mechanism of exchange has been studied with radioactive cobalt ions in solutions into which

[1] Manuscript received January 9, 1951. This paper prepared for delivery before the Buffalo Meeting, October 11 to 13, 1950.

[2] The work of Haissinsky (7) and his collaborators with radioactive solutions and their study of electrodeposition from dilute solutions deserves special attention.

various metals with different surface treatments were immersed in the presence and absence of oxygen. The acquired radioactivities were measured and the distribution of radioactive cobalt on the surfaces shown by means of autoradiographs. Calculations have also been made of the magnitudes of the local cell currents on the metal surfaces.

TABLE I

Specimen	Surface treatment	Time of exchange	Activity counts/min		Equiv. current coulombs/sec/cm²		Atom layers/cm²	
			O_2—absent	O_2—present	O_2—absent	O_2—present	O_2—absent	O_2—present
		min						
Cobalt	Etched	1	—	2,600	—	2.8×10^{-4}	—	0.26
Cobalt	Etched	5	9,600	20,300	2.1×10^{-6}	4.4×10^{-6}	0.96	2.03
Cobalt	Etched	30	11,800	32,000	4.3×10^{-7}	1.15×10^{-6}	1.18	3.20
Cobalt	Etched	120	16,000	50,100	1.45×10^{-7}	4.5×10^{-7}	1.60	5.01
Cobalt	Etched	1440	17,700	52,200	1.3×10^{-8}	3.9×10^{-8}	1.80	5.22
Cobalt	Etched	2880	20,300	40,500	7.6×10^{-9}	1.5×10^{-8}	2.03	4.05
Cobalt	Ground 000	120	24,200	53,300	2.2×10^{-7}	4.8×10^{-7}	2.42	5.33
Cobalt c-r*	Etched	120	10,500	44,500	9.5×10^{-8}	4.0×10^{-7}	1.05	4.45
Nickel	Etched	120	2,350	47,000	2.1×10^{-8}	4.2×10^{-7}	0.235	4.70
Nickel	Etched (HF)	120	8,600	49,000	7.8×10^{-8}	4.4×10^{-7}	0.86	4.90
Iron	Etched	15	32,200	70,000	2.3×10^{-6}	5.0×10^{-6}	3.22	7.00
Iron	Etched	120	53,400	103,400	4.8×10^{-7}	9.3×10^{-7}	5.34	10.3
Iron	Ground 000	120	12,800	106,000	1.15×10^{-7}	9.5×10^{-7}	1.28	10.6

* c-r denotes cold-rolled.

TABLE II

Specimen	Surface treatment	Time of exchange	Activity counts/min		Equiv. current coulombs/sec/cm²		Atom layers/cm²	
			O_2—absent	O_2—present	O_2—absent	O_2—present	O_2—absent	O_2—present
		min.						
18–8 Stainless	Etched	120	1,700	550	1.5×10^{-8}	4.9×10^{-9}	0.17	0.055
18–8 Stainless	Etched air 5 min	120	—	340	—	3.1×10^{-9}	—	0.034
18–8 Stainless	Etched air 1 day	120	—	190	—	1.7×10^{-9}	—	0.019
18–8 Stainless	Etched scratch	120	—	920	—	8.1×10^{-9}	—	0.09
18–8 Stainless	Ground 000	120	140	16,500	1.2×10^{-9}	1.5×10^{-7}	0.014	1.64
Titanium	Etched	120	3,400	640	3.1×10^{-8}	5.7×10^{-9}	0.34	0.064
Titanium c-r*	Etched	120	360	720	3.2×10^{-9}	6.5×10^{-9}	0.036	0.072
Aluminum, cast	Etched	120	32,000	140	2.9×10^{-7}	1.3×10^{-9}	3.2	0.014
Silver		120	0	0	0	0	0	0
Platinum		120	45	125	4.1×10^{-10}	1.1×10^{-9}	0.0045	0.0125
Copper	Etched	120	5,700	4,400	5.1×10^{-8}	3.9×10^{-8}	0.57	0.44
Copper	Polished	120	1,800	1,600	1.6×10^{-8}	1.4×10^{-8}	0.18	0.16
Cu-Ag-Cu	Ground 000	120	—	0	0.9×10^{-10}	0	0.001	0
Cu-Pt-brass	Ground 000	120	—	25,600	—	2.3×10^{-7}	—	2.56
Cu-8% Ag	Ground 000	120	—	3,400	—	3.1×10^{-8}	—	0.34
Cu-8% Ag	Etched	120	—	15	—	1.3×10^{-10}	—	0.0015

* c-r denotes cold-rolled.

Experimental

Materials

The radioactive cobalt isotope, Co^{60}, used in these experiments has a half-life of 5.3 years and emits beta radiation of 0.31 mev and two monoenergetic gamma radiations of 1.16 and 1.30 mev. The metals used were: cobalt, nickel, iron, aluminum, titanium, 18–8 stainless steel, platinum, silver, copper, and couples consisting of copper/brass, copper/8% silver-copper, copper/platinum/brass, and copper/silver/copper. The couples were made by welding under pressure in hydrogen at high temperature. The surface treatments given prior to immersion in the solutions are included in Tables I and II.

Solutions

The activity of the solutions of cobalt sulfate used in these experiments was about 50,000 counts per minute/cm³. For experiments in the absence of oxygen, the solutions were pumped out and placed under an atmosphere of pure nitrogen.

Counting

The active specimens were counted in a Tracerlab Autoscalar using an argon-filled, self-quenching Tracerlab tube having a window thickness of 1.5 mg/cm². The specimens were thick enough that the backscattering was at its saturation value and, therefore, dependent only on the material of the specimen. Coincidence corrections were also made on the counts obtained. One atom layer of the active cobalt gave 3120 counts per minute per cm², which was equivalent to 1.78×10^{-7} grams of cobalt.

Apparatus

The cell used for carrying out the experiments is shown in Fig. 1. It was possible to evacuate and fill the cell with purified nitrogen through a three-way tap, T. The specimen was placed in the shallow glass dish, A, attached to the glass rod, B, by means of

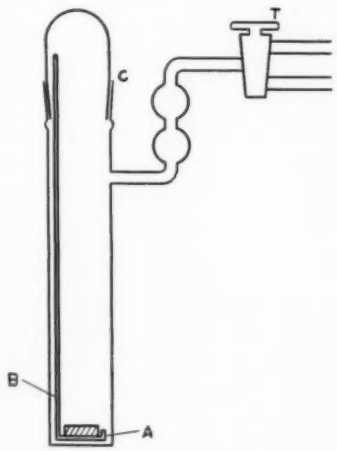

FIG. 1. Diagram of cell

which it could be placed in or removed from the solution. The ground-glass joint, C, facilitated the rapid placing of the specimens into the cell in a stream of pure nitrogen gas. The experiments were carried out in a thermostat at a temperature of 30°C.

Procedure

The specimens were annealed in hydrogen for four hours at 600°C and slowly cooled in the furnace. In experiments where oxygen was present, they were exposed to the air for a short time and placed in solutions containing the radioactive cobalt. In experiments where oxygen was absent, the specimens were etched in acids which removed any oxide films present on the surfaces, and immediately washed in alcohol while still wet with the etchant. Then, before the alcohol had evaporated off completely, the specimens were placed in the solutions in a stream of nitrogen, and the cells evacuated and refilled with nitrogen. The efficiency of the etchant for each metal (except aluminum) was easily tested by first heating a piece of the metal in air until interference tints were formed. The tinted specimen was then placed in the various etchants to find the one which rapidly removed the oxide, as could be observed from the disappearance of the color. In the case of the distorted surfaces, the method used was to emery the specimen under alcohol, then wash with alcohol and immediately place into the cell. These methods were shown to be efficient by means of tests carried out with stainless steel. It is known that the resistance of stainless steels to attack in a solution of bromine in alcohol is due to the oxide film present on the metal (5). If the oxide film is scratched, attack takes place at that point. A stainless steel specimen that had been treated by either of the two methods described above was uniformly attacked over the whole surface when placed in alcoholic solution of bromine, showing that these methods served their purpose adequately.

After the required times of immersion in the solutions, the specimens were removed and washed in a running stream of distilled water for five minutes. They were then washed with alcohol, dried in a stream of air, and placed in a dessicator. The acquired activities were measured in the counter, and autoradiographs were obtained on spectrographic plates. The exposures necessary for obtaining a reasonable darkening of the emulsion varied from less than an hour for the highly active samples, to over a day for the weakly active specimens. The usual precautions (6) that are necessary in autoradiography were taken in order to avoid spurious results. Some metals cause a fogging action on photographic emulsions due to the hydrogen peroxide produced in the corrosion of their freshly abraded surfaces. This actinic effect may be overcome by insuring the absence of moisture on the metal surface during exposure. Pressure, abrasion, and shock also render certain emulsions developable. The autoradiographic patterns were compared with the appearance of the corresponding metal surfaces.

RESULTS

Cobalt specimens.—The first specimen used had large grains and was thermally etched by heating at 1200°C in hydrogen for one day. The resulting rough surface was lightly ground on 000 emery paper so as to distort the surface only at the parts standing out of the surface. The resulting surface consisted partly of areas which were distorted and partly of the annealed stress-free areas. After exchange, the autoradiograph showed remarkably good correlation between the areas that had acquired

activity and the annealed areas on the specimens (Fig. 2). There was little pick-up of active cobalt ions in the distorted regions; practically all the

FIG. 2. Autoradiograph of partly distorted cobalt specimen. The polished surface was first thermally etched at 1200°C in hydrogen. It was then lightly ground on 000 emery so as to distort the elevated parts. The autoradiograph of the exchanged surface is an exact replica in that the dark areas correspond to the undistorted (cathodic) parts and the white areas correspond to the distorted (anodic) corroded parts of the surface. 3×.

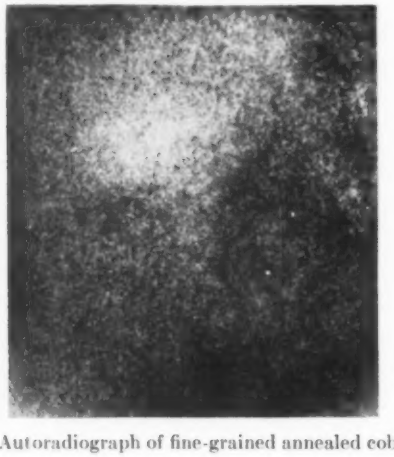

FIG. 3. Autoradiograph of fine-grained annealed cobalt. 2×

active cobalt ions had deposited on the cathodic annealed areas.

The fine-grained cobalt specimens showed an even distribution of activity on the surface (Fig. 3), since the resolution was not sufficient to show up the grain size of the specimens unless the autoradiographs were magnified. The activity increased with time of immersion in the solution to an asymptotic value in the absence of oxygen, but in the presence of oxygen it increased to a maximum and then decreased. The increase of activity with time of immersion was greater in the presence of oxygen. The magnitudes of the currents on the specimens immersed in the solutions, which were calculated from the corresponding activities by means of Faraday's law, increased to a maximum value within five minutes of immersion and then decreased with time. The value of these currents varied from about 5 to 0.01 microamp/cm^2. The maximum number of atom layers averaged over the whole surface of the specimens was about 5 atom layers/cm^2 in the presence of oxygen and about 2 atom layers/cm^2 in the absence of oxygen. For an equal time of exchange, a cold-rolled specimen showed less activity than the annealed.

Nickel—In the absence of oxygen, the nickel acquired much less activity than cobalt, whereas in the presence of oxygen there was little difference in the activities. The use of different etchants resulted in different acquired activities, the effect being especially marked in the absence of oxygen.

Iron—The activities acquired by iron were far greater than with cobalt for equal times of immersion in the solutions. The influence of oxygen and the values of maximum local cell currents were the same as in the case of cobalt. The effect of grinding the surface, however, was different in that it resulted in an appreciable decrease in the acquired activity in the absence of oxygen.

18-8 Stainless steel—With etched specimens the amount of exchange was much greater in the absence of oxygen. In the presence of oxygen, pre-exposure to air caused a decrease in activity, but scratching the surface caused a great increase in activity. In the absence of oxygen, a ground surface acquired far less activity than an etched surface.

Titanium—The annealed specimen acquired a far greater activity than the cold-rolled in the absence of oxygen, whereas the reverse was true in the presence of oxygen. The presence of oxygen also decreased the acquired activity.

Aluminum—The specimens of aluminum used were from a casting, and consisted of about equal areas of large columnar crystals and small equiaxed crystals. In the absence of oxygen, the activity acquired was even greater than in the case of cobalt for the same period of immersion in the solution. The autoradiographic patterns (Fig. 4) followed the general pattern of the surface crystal structure: namely, there was a zone simulating the columnar crystals, and a more evenly darkened area corre-

sponding to the equiaxed crystals. In the presence of oxygen, the activity acquired was very small.

Silver—No measurable activity was acquired by silver, either in the presence or absence of oxygen.

Platinum—A small but measurable activity was acquired by platinum, which was greater in the presence of oxygen.

Copper—The etched specimens of copper revealed a circularly oriented surface structure which followed

FIG. 4. Autoradiograph of cast aluminum specimen. The lower one third of the figure corresponds to columnar grains and the upper two thirds correspond to equiaxed grains on the metal surface. 2×.

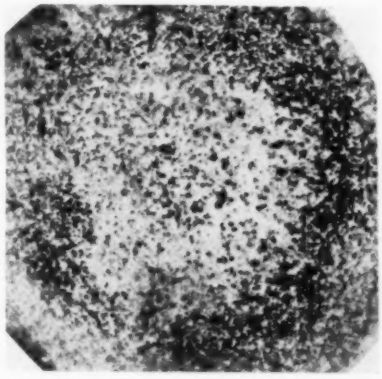

FIG. 5. Autoradiograph of copper, showing the influence of preferred orientations (caused by machining of the sample prior to annealing) upon distribution of exchange. 2×.

the pattern of previous machining lines. The latent distortion produced during the machining operation had influenced the recrystallization during the annealing of the polished specimens. The activity acquired during exchange was concentrated on crystals with certain preferred orientations, and resulted in an autoradiographic pattern (Fig. 5) which was similar to the general crystalline structure of the surface of the specimens. Metallographic polishing caused a decrease in the activity. The influence of oxygen was slight.

When placed in contact with silver, however, the copper acquired no measurable activity, either in the presence or absence of oxygen.

When placed in the solution, a couple consisting of copper and brass, and also one with a thin foil of platinum placed between the copper and brass, corroded in distinct regions of appreciable area. The

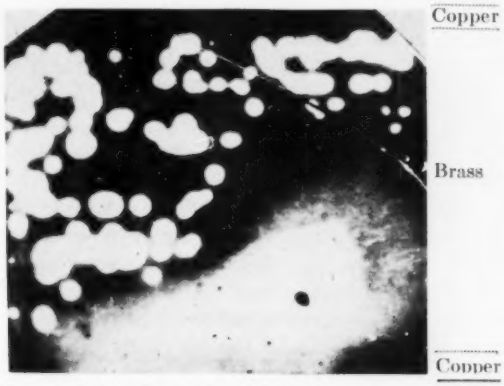

FIG. 6. Autoradiograph of brass/copper couple. The white areas, where no exchange has taken place, correspond exactly to parts of the surface where corrosion had taken place. 2×.

FIG. 7. Autoradiograph of copper/platinum/brass couple, showing the influence of intense local cell action upon exchange. The white areas are exact replicas of the corroded parts of the surface. (The platinum foil was in the center of the lower white area.) 2×.

autoradiographs of such specimens (Figs. 6 and 7) were excellent replicas of the exchanged surface, in that the corroded parts showed no activity whatever and the bright, uncorroded areas showed high activity.

A couple consisting of copper with an alloy of copper containing 8 per cent silver acquired an activity which was concentrated on the Cu-8% Ag part of the couple. However, if the couple was first etched before being placed in the active solution,

then practically no activity was acquired. The etching treatment had depleted the Cu-8% Ag part of copper, so that this half of the couple was covered with a layer of silver, and, as in the case of the Cu-Ag couple, no cobalt remained plated on the silver.

Discussion and Conclusions

The results obtained with the various metals and alloys can be generalized as follows:

1. The radioactivity acquired by metal surfaces in ionic solutions containing radioactive ions is governed by the distribution of local anodes and cathodes on the metal surface. This local cell action results in the cations being deposited on the cathodic areas.

2. The influence of oxygen depends upon the nature of the oxide films formed on the metals. If the oxide film is not very protective, the oxygen increases the activity acquired by the metal by acting as a depolarizer. On the other hand, a protective oxide film greatly decreases the activity by limiting the areas where electrolysis can take place.

3. The orientation of the grains markedly affects the distribution and amount of activity that is acquired. Cold-working, which is known to confer preferred orientation to the crystal structure, results in a decreased activity.

4. The platability of the radioactive ions on the cathodic parts of the surface is also a factor that greatly influences the activity remaining on the exchanged specimen. Thus, silver on which cobalt is difficult to plate directly acquires no measurable activity, even when placed in contact with copper so as to make it definitely cathodic.

5. The position of the metal in the electromotive force series in the particular solution with respect to the radioactive ion in solution affects the activity acquired. Metals more noble than the metal ion in solution acquire less activity than base metals (in the absence of oxide films). This is to be expected, because in the latter instance electrochemical displacement can also take place, while deposition of the noble ion on cathodic regions of the base metal greatly increases the local cell action by increasin the potential difference on the metal surface.

6. The magnitude of the currents present on metal surfaces immersed in solutions can be calculated from the acquired activity if radioactive ions are present. The maximum value of these currents has been estimated to be of the order of several micr amp/cm^2.

The influence of time, temperature, and *p*H and the nature of the radioactive ions present in the solution are being studied to throw further light on the behavior of metals in ionic solutions.

Acknowledgment

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the Journal.

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Electrolytic Determination of Cadmium in Zinc Sulfide-Cadmium Sulfide Phosphors[1]

ROBERT BASTIAN, RICHARD WEBERLING, AND FRANK PALILLA

Sylvania Electric Products Inc., Kew Gardens, New York

ABSTRACT

A rapid electrolytic method for determining cadmium in zinc sulfide-cadmium sulfide phosphors is presented. From 0.2 to 0.7 gram of cadmium is plated from a sulfuric acid potassium bisulfate solution containing up to 3 grams of zinc. Cadmium deposition is not quite complete but the amount remaining in solution is so nearly constant that a correction can be made for it. When this is done an average accuracy and precision of about one part per thousand is obtained.

INTRODUCTION

The widespread use of zinc sulfide-cadmium sulfide phosphors makes the development of a rapid method suitable for routine analysis of these materials highly desirable. For many purposes it is sufficient to analyze for cadmium content. The common procedure is to separate cadmium from zinc by precipitating the former with hydrogen sulfide (1). The cadmium sulfide is then usually redissolved and cadmium determined electrolytically (1). The object of this paper is to present a method for the electrolytic determination of cadmium in the presence of zinc. The procedure is simple, can be completed in less than three hours, and yields accurate results.

The many attempts which have been made to achieve an electrolytic determination of cadmium in the presence of zinc have been reviewed by Hammond (4). Most of the recent work has involved very accurate control of the cathode potential [reviewed by Diehl (3)]. Although this approach is promising, rather complex equipment is required, and as yet no completely satisfactory procedure has resulted. Using a conventional plating procedure and a dilute sulfuric acid or aqueous sodium bisulfate medium, Treadwell and Guiterman (7) reported quantitative results on weights of cadmium up to 0.2 gram in the presence of as much as 4.6 grams of zinc. However, several more recent workers (2, 4, 5) have been unable to plate cadmium completely from dilute sulfuric or even buffered acetic acid media. Slomin (6) states that cadmium can be separated from zinc in a sulfuric acid solution containing potassium bisulfate, but gives no indication of the accuracy of the method.

Much of the work reported suffers from the rather low weights of cadmium plated, making small errors in weight represent large percentage errors.

EXPERIMENTAL

Apparatus and Materials

The following apparatus and materials were used:

Sargent-Slomin electrolytic analyzer.

Sargent S29632 platinum anodes, rotating (460–550 rpm).

Sargent S29672 platinum cathodes. These were plated with 0.1 to 0.2 gram of copper prior to each analysis.

C. P. grade zinc sulfate, potassium bisulfate, nitric and sulfuric acids.

Cadmium metal (General Chemical Company, Code 1478).

Triple vacuum distilled cadmium metal (New Jersey Zinc Company, Palmerton, Pennsylvania). This metal was analyzed spectrographically and found to be of high purity.

Preliminary Investigation

Several analyses were carried out in an aqueous sulfuric acid, potassium bisulfate medium containing 0.2–1 gram of cadmium (General Chemical) and up to 3 grams of zinc. The solution volume was kept at about 200 ml while the effect of varying current, acidity, and potassium bisulfate content were studied. No attempt was made to control the voltage. In most of the tests somewhat low results were obtained for cadmium tending to confirm References 2, 4, and 5, and when attempts were made to rectify this by increasing the current or potassium bisulfate content or by decreasing the acidity, zinc was codeposited.

Under certain easily controlled conditions, however, the results for cadmium were always low by

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very nearly 2 mg regardless of the amounts of zinc and cadmium present. Spectrographic analysis of the deposits obtained indicated that they consisted of very nearly pure cadmium. In one experiment, two electrodes previously plated with 0.2 gram of cadmium were inserted in solutions containing 3 grams of zinc but no cadmium. After electrolyzing, both electrodes lost very nearly 2 mg in weight. On the basis of these tests it was decided to adopt the conditions and apply a constant correction for residual cadmium. Such a correction was suggested by Hammond (4) in his work with a buffered acetic acid bath, but the requirements were more rigorous and the weights of cadmium and zinc 0.1 gram or less.

TABLE I. *Determination of correction for residual cadmium*

Zinc present	Cadmium taken	Cadmium plated	Difference	Error in parts per thousand using 1.9 mg correction
g	*g*	*g*	*mg*	
3	0.1970	0.1950	2.0	−0.5
3	0.2013	0.1994	1.9	0.0
3	0.2013	0.1989	2.4	−2.5
1.5	0.2423	0.2406	1.7	0.8
3	0.2543	0.2519	2.4	−2.0
None	0.2987	0.2966	2.1	−0.7
1.5	0.3302	0.3286	1.6	0.9
None	0.3613	0.3583	3.0	−3.0
3	0.3793	0.3577	1.6	0.8
None	0.3930	0.3910	2.0	−0.3
0.6	0.3967	0.3947	2.0	−0.3
3	0.4334	0.4325	0.9	2.3
0.6	0.4401	0.4378	2.3	−0.9
None	0.4548	0.4526	2.2	−0.7
0.6	0.4754	0.4739	1.5	0.8
1.5	0.4861	0.4852	0.9	2.1
3	0.5119	0.5103	1.6	0.6
3	0.5441	0.5418	2.3	−0.7
1.5	0.6120	0.6110	1.0	1.5
3	0.6180	0.6166	1.4	0.8
1.2	0.6208	0.6188	2.0	−0.2
3	0.6723	0.6699	2.4	−0.7
3	0.6758	0.6736	2.2	−0.4
Average			1.9 ± 0.4	±1.0

Accurate Determination of Correction

Individual samples of triple vacuum distilled cadmium were rinsed with acetone, dried for a few moments at 110°C, and weighed. These were placed in 250-ml covered beakers and in most cases heated strongly with about 7 ml of concentrated sulfuric acid to effect solution. A few samples were dissolved in nitric acid which was expelled by adding sulfuric acid and evaporating twice to sulfuric acid fumes, but this evaporation was tedious and subject to bumping. After the cadmium was converted to the sulfate, solutions were concentrated to about 5 ml, estimated by comparison with a similar beaker containing this volume of sulfuric acid. This is sufficiently accurate because the acidity is not critical in the range of 3 to 5 ml. If there is less than 3 ml there is danger of zinc deposition, and if more than 7 ml, somewhat more cadmium tends to remain in solution.

After the cadmium was dissolved zinc was added by aliquot from a zinc sulfate stock solution, and in a similar way 5.7 grams of potassium bisulfate were added to each solution. Solutions were cooled to room temperature, diluted to about 200 ml by comparison with a similar beaker containing this volume of water, and electrolyzed by an analyst who did not know the weights of cadmium taken.

The current was set initially at 0.9 amp, and the electrolysis continued for 1½ hr. Usually the current dropped 0.2 to 0.3 amp during the electrolysis. This was restored to 0.9 amp about 15 min before the end of the electrolysis (with some solutions it was restored a few times as the electrolysis progressed). The initial voltage varied from 2.8 to 3.4 v, decreasing in general, but not invariably, with increasing cadmium concentration.

The electrodes were withdrawn with the current on and rinsed immediately with distilled water from a wash bottle. They were then dipped into two 75-ml changes of distilled water contained in 100-ml beakers, then in about 75 ml of methanol, and then dried at 110°C for a few moments, cooled, and weighed.

Results are shown in Table I. The cadmium plated is lower than the cadmium taken in all cases, the average discrepancy being 1.9 ± 0.4 mg which is, therefore, the best value for the correction. If this value is used to correct all of the results in column 3, the resultant errors, expressed in parts per thousand, are given in column 5. The maximum error is −3.0 parts per thousand and the average error ±1 part per thousand. Only two of the 23 values would be better without the correction and these only by 0.1 mg, which is hardly significant.

Nature of Deposits

The deposits had a tendency to show a slight roughness along the reinforced areas of the electrodes. With very rough handling bits of the deposit could be dislodged, but in cases where zinc was present in the original solution there was no danger of so doing except by a deliberate attempt. In those four cases (see Table I) where zinc was absent, these rough areas assumed a crystalline character, and in two of those instances (0.3613 and 0.4548 gram of cadmium taken) crystals of cadmium were projecting at various angles from the base of the electrode, which could be dislodged by tapping the electrode. With these two samples there was definite danger of

dislodging some of the deposit, although it was not actually observed. (In all the work electrodes were dried and carried in a wooden block into which were drilled small holes. Electrodes were inserted stems down to avoid contact of the deposit with any surface.) It is curious that the adherence of the cadmium deposit is greatly improved by the presence of zinc in the electrolyte, but this point was not subjected to further investigation because in subsequent analyses on phosphors good adherence was always obtained.

Minimum Safe Weight of Cadmium

The amount of cadmium in the solution to be plated under the specified conditions should be not less than 0.2 gram, because drawing 0.9 amp the voltage might rise to the point of depositing zinc. Some determinations using 0.1 gram of cadmium and 3 grams of zinc yielded expected results, but in other cases as much as 1 gram of zinc plated out. In some cases this clearly could be attributed to a high voltage (any reading above 3.5 may be viewed with suspicion), but in other cases the voltage was not exceptionally high. The situation is probably complicated by polarization effects. Perhaps the difficulty could be avoided by plating at a lower amperage but this would result in a higher residual cadmium content.

If it is necessary to plate less than 0.2 gram of cadmium this can be done by employing an electrode previously plated with at least 0.2 gram of cadmium (on top of the copper). Under the conditions of the electrolysis zinc will not deposit on such an electrode whereas cadmium will deposit as usual. (The minimum safe weight of cadmium will no doubt depend on the type of electrodes used. These considerations apply only to these particular electrodes.)

In practical phosphor analysis one can usually take a sample large enough to yield at least 0.2 gram of cadmium so that the copper plated electrodes can be used safely. A sample containing about 0.4 gram is recommended to reduce the effect of the uncertainty in the correction for residual cadmium.

Analysis For Residual Cadmium

To determine whether the 1.9-mg correction derived empirically actually represented residual cadmium some analyses were performed on electrolyzed solutions from Table I. The term "residual cadmium" refers not only to cadmium which could not be plated from solution, but also to the cadmium which might have been redissolved by the water used to wash the deposit free of electrolyte. Tests showed that the two 75-ml portions of rinse water used prior to the alcohol dip contained an average of about 0.3 mg of cadmium per determination. (No significant amounts of cadmium were found in the alcohol.) In analyzing for residual cadmium, therefore, these two portions of rinse water were added to the electrolyzed solutions (which already contained the initial electrode washings). Analyses were performed by a spectrophotometric method and, on the basis of results obtained on similar solutions containing known amounts of cadmium, are believed accurate to ±0.1 mg of cadmium.

The four samples containing 1.5 grams of zinc (see Table I) were analyzed in this way. The residual cadmium found varied from 1.8 to 2.2 mg, and averaged 2.0 mg, thus verifying the correction found empirically.

This is true in spite of the fact that the last two samples gave rather high results when the correction was applied. Therefore, high results are probably not due to an uncertainty in residual cadmium, but rather to contamination of the deposit. Such contamination could be due to zinc metal, or to the occlusion of small amounts of salts or hydrogen gas. It could also be due to a slight oxidation of the deposit during drying, although no visual evidence of this presented itself.

TABLE II. *Analysis of phosphors, percentage of cadmium sulfide*

Sample No.	Analyst 1	Analyst 2	Analyst 3	General average	General average deviation, parts per thousand
I	28.08	28.01			
	28.06	28.04	28.07		
Average	28.07	28.03		28.05	±0.8
II	32.04	31.99			
	32.05	32.06			
Average	32.05	32.03		32.04	±0.6
III		13.04			
		13.02	13.01		
Average		13.03		13.02	±0.8
IV		11.35			
		11.38			
Average		11.37		11.37	±1.3
V	54.53	54.41	54.31		
	54.54	54.34	54.46		
Average	54.54	54.38	54.39	54.43	±1.4

Sample No.	Approximate sample wt taken	Approximate wt of Cd plated
	g	*g*
I	1.9–2.0	0.43–0.44
II	1.6–2.0	0.39–0.50
III	2.0–3.7	0.20–0.37
IV	4.6*	0.41
V	1.0–1.4	0.43–0.58

* 15 ml of concentrated sulfuric acid used to dissolve sample.

Analysis of Phosphors

A weighed sample was placed in a 250-ml beaker and treated with 10 ml of concentrated sulfuric acid.[2] The sample was heated gently until decomposed, then strongly until most of the sulfur was oxidized or volatilized and the salts were white. The solution was concentrated to about one half its original volume. In most cases a small amount of free sulfur, evident as small molten globules in the beaker or on the watch glass, remained after this treatment. No attempt was made to drive off these last traces. After cooling, 50 ml of water were added, the solution heated to boiling, and filtered through Whatman #40 paper into a 250-ml beaker, washing with hot water. Then 5.7 grams of solid potassium bisulfate were added, the solution cooled to room temperature in running water, diluted to 200 ml, and plated as before. The 1.9-mg correction was applied in each case. The results are summarized in Table II.

The greatest discrepancy between the average values for two observers is 2.9 parts per thousand in Sample V. General average deviations vary from ± 0.8 to ± 1.4 parts per thousand.

Discussion

It is important to observe that if enough phosphor is taken to yield about 0.4 gram of cadmium, an accuracy sufficient for many purposes will be obtained even without applying any correction for residual cadmium. These results will always be low, however, and can be improved considerably by applying the correction established in this paper.

The effect of impurities or activator metals such as silver, which might deposit with cadmium, have not been considered because in the materials of interest their percentages were very low. If such is not the case the effect of these metals should be taken into account.

[2] Solution can be effected with hydrochloric acid, but the subsequent evaporation to sulfuric acid fumes is subject to severe bumping. Dilute sulfuric acid was found unsatisfactory.

Acknowledgment

Thanks are expressed to Vincent Brophy for performing spectrographic analysis referred to herein.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the Journal.

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Current Distribution over a Cylinder with Hemispherical Ends[1]

SIDNEY BARNARTT

Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania

ABSTRACT

The purpose of this study was to design an electrode (anode) that would yield relatively uniform primary current distribution over a cylinder with hemispherical ends (cathode). The designing was carried out using the electrolytic trough method of mapping equipotential surfaces between electrodes. Cathode current distributions derived from the equipotential maps were compared with the distributions of electrodeposited chromium. Deviations between the two distributions, which are a measure of the effect of anode polarization during chromium plating, were generally small. Primary cathode distributions with maximum deviations from the mean of about 10 per cent are readily obtainable using relatively simple anode geometries.

INTRODUCTION

The primary purpose of this investigation was to design an electrode which, from geometrical considerations only, would yield relatively uniform distribution of current over the surface of a cylinder with hemispherical ends. The designing was carried out empirically by mapping equipotential surfaces in an electrolytic model. Current distributions derived from the equipotential maps were compared with the distributions of chromium electrodeposited from chromic acid solution.

For most studies requiring uniform current distribution, accurate electrode geometries may be sectioned from one of the three mathematical cases: infinite parallel planes, infinite concentric cylinders, and concentric spheres. The requirements for duplicating these cases electrolytically have been discussed by Kasper (1). None of the three cases, however, was suited to the application which prompted the present study. This application involved the electrodeposition of metals, such as chromium, with uniform current density over the *entire* surface of a test specimen. Test specimens of simple planar or cylindrical geometry are unsuitable because it is difficult to obtain the same current density over the ends as over the principal surfaces. In order to use spherical test specimens, the area on which electrical contact is made must be moved randomly a large number of times during electrolysis; the cell design would be very complex. To the writer's knowledge, current distribution over a cylinder with hemispherical ends has not been studied heretofore. If uniform current distribution could be obtained over a specimen of this shape, the specimen could be electroplated in halves with a thin overlap band around the middle of the cylinder. Thus all the metal coating would be deposited at the same current density, the small area of discontinuity having double coating thickness.

The cylinder with hemispherical ends, to be referred to hereinafter as the cathode, can be treated as a combination of concentric cylinders and concentric spheres. On this basis the other electrode, to be referred to as the anode, would consist of a cylindrical tube opposite the cylindrical area of the cathode and hollow hemispheres opposite the hemispherical ends, the tube and hemispheres being separated by thin, insulating disks. Variations in cathode current density opposite the insulators could be made relatively small. In order to maintain the same potential over the entire anode, the tubular and hemispherical portions would have to have different radii; conversely the radii would be the same only if these portions were maintained at different potentials.

For simplicity, therefore, a single equipotential anode was sought. This was designed using the so-called "electrolytic trough" method, introduced by Fortescue and Farnsworth (2) and improved by Estorff (3) who substituted a-c voltages to reduce polarization errors. This method yields a map of the equipotential surfaces between the electrodes, from which the current distributions over the surfaces of the electrodes may be determined. An electrolytic model of the selected cathode and an anode of arbitrary initial shape was constructed, and the equipotentials mapped. From the information given by the map the anode was reshaped for better current distribution, a new map was obtained, and the cycle was repeated several times.

[1] Manuscript received February 12, 1951. This paper prepared for delivery before the Detroit Meeting, October 9 to 12, 1951.

Procedure and Results

Potential Mapping

Since a cylinder with hemispherical ends has an axis of symmetry, any plane containing the axis will display every typical equipotential line. Only one quadrant of such a plane need be mapped out. A wedge-shaped model of the system may be sectioned out, and represented physically by two conductors dipping into an electrolyte contained in a tank with a sloping bottom (4). The "shore line" in the tank is the axis of symmetry.

Fig. 1 presents a diagram of the apparatus used. The electrical circuit is essentially an a-c Wheatstone bridge. A movable probe, dipping just below the surface of the electrolyte, is connected to the potentiometer through a detector. The detector

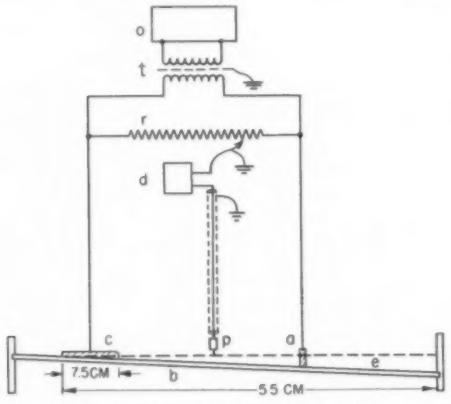

Fig. 1. Apparatus for mapping equipotentials. *a*—Anode, oxygen-free high-conductivity copper; *b*—glass bottom of tank, 6° slope, 90 cm long; *c*—cathode, oxygen-free high-conductivity copper; *d*—detector, Ballantine a-c voltmeter model 300; *e*—electrolyte, 0.005% potassium dichromate; *o*—oscillator; *p*—probe; *r*—potentiometer; *t*—audio transformer with interwinding shield.

shows minimum voltage whenever the probe is on the equipotential line corresponding to the setting of the potentiometer. In this way equipotential lines are readily traced out in the plane represented by the top surface of the electrolyte. The probe was carried by an accurate well-balanced pantograph, by means of which traces of the equipotential lines were made on a drawing board near the tank.

The conductors in the model should be curved about the axis of symmetry. Since the angle of the wedge was small (6 degrees), the conductors can be bent to shape from flat copper strip with little displacement of the equipotentials except very near the distorted electrodes. Since only the equipotentials near the cathode were important, copper strip was used for shaping the anode while the cathode was accurately machined out of solid copper. The dimensions selected for the latter were 7.5 cm radius (R) and 15 cm ($2R$) cylindrical length.

For accurate spotting of equipotentials near the axis of symmetry, the contact angle between the electrolyte and the bottom of the tank should approximate the angle of the wedge. To accomplish this, a line was drawn with a wax crayon where the shore line was desired. The solution was encouraged to wet the glass bottom of the tank by lightly grinding the glass at the shore side, then running a glass rod which had been dipped in a dilute wetting agent along the shore. By means of leveling screws under the tank, the solution was brought up to the wax line and then lowered until the meniscus vanished. Sharp shore lines were secured in this manner.

With the circuit shown in Fig. 1, pickup was effectively eliminated. The combination of copper electrodes in 0.005 per cent potassium dichromate solution was found to yield very low minimum voltages. In mapping the equipotentials, 5 volts across the electrodes at 1000 cycles/sec were used; the minimum readings were approximately 1 mv, increasing to 5 mv as the shore line was closely approached. Thus the equipotential lines were sharply positioned.

Potential gradients at the surface of the cathode were determined from the equipotential lines representing 5, 10, 15, and 20 per cent of the total potential drop. In order to simplify the calculation of the gradients, it was assumed that these lines represented concentric cylinders opposite the cylindrical portion of the cathode and concentric hemispheres opposite the spherical portion. For the cylindrical case:

$$V = a - b \log r \qquad \text{(I)}$$

and

$$dV/dr = -b/r \qquad \text{(II)}$$

where V is the potential of the line and r its radius. For the spherical case:

$$V = c + d/r \qquad \text{(III)}$$

and

$$dV/dr = -d/r^2. \qquad \text{(IV)}$$

Hence plots of V against log r and $1/r$ respectively should be linear, the slopes of the lines being a measure of the potential gradients. It was found that these plots were linear within experimental error, except very near the junction of the cylindrical and hemispherical portions of the cathode where appreciable deviations were expected. The 0 per cent equipotential line (i.e., the cathode position) was omitted from the plots in order to minimize possible polarization errors; this is discussed in the next section.

The potential gradients in the electrolyte at the surface of the cathode are a measure of the current distribution over this surface, since

$$i = -\kappa dV/dr \qquad (V)$$

where i is the current density and κ is the specific conductance of the medium. Table I presents measured gradients for four anode configurations that gave relatively uniform distribution over the cathode; the anode geometries and equipotential maps

TABLE I. *Potential gradients at the surface of the cathode*

Position on cathode		Potential gradient, %/cm			
		Anode			
No.	Distance from hemispherical end along axis, cm	*A*	*B*	*C*	*D*
1	0.1	16.7	16.8	21.2	16.9
2	1.5	16.7	17.3	22.3	17.5
3	4.0	17.2	18.5	25.0	19.6
4	6.5	17.1	18.7	25.2	20.0
5	9.0	15.3	15.6	21.0	17.9
6	14.5	15.7	16.0	20.4	19.3
7	20.5	15.9	16.3	20.1	20.1
Mean gradient*.....		16.2	16.7	21.6	19.2
Maximum deviation from mean, %.....		6	11	17	12

* Mean ordinate of the gradient vs. position curve.

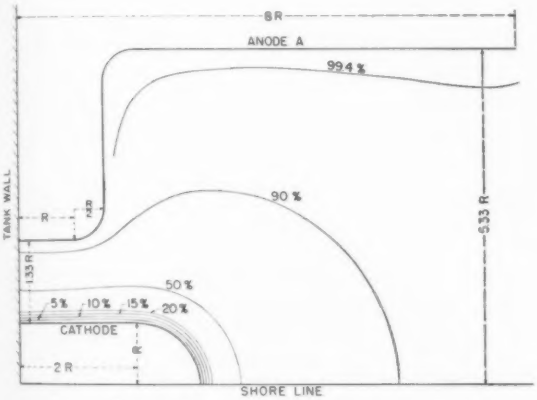

FIG. 2. Potential map, anode *A*

are shown in Fig. 2 to 5. Most of the gradients of Table I are probably accurate to ±2 per cent. Near the shore line, position 1, the capillary rise of the electrolyte on the probe, and the relatively high local concentration of wetting agent in the solution, may have added an appreciable error. Near the junction of the cylinder and hemisphere, positions 4 and 5, departure of the equipotentials from concentric cylindrical and concentric spherical arrangement may also add to the gradient error.

A-C Polarization in the Copper-Dichromate System

Polarization at the copper electrodes during the potential mapping would cause displacement of the equipotential lines and hence additional error in the gradient. A study of a-c polarization at copper electrodes in 0.005 per cent potassium dichromate solution was carried out to evaluate polarization errors. The Wheatstone bridge arrangement of Fig. 1 was

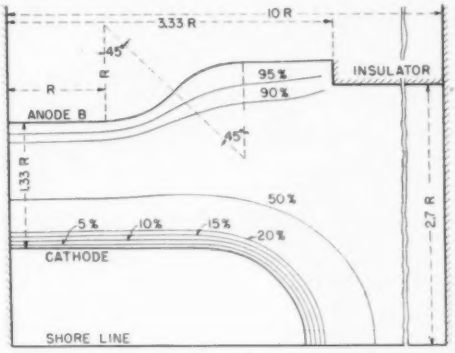

FIG. 3. Potential map, anode *B*

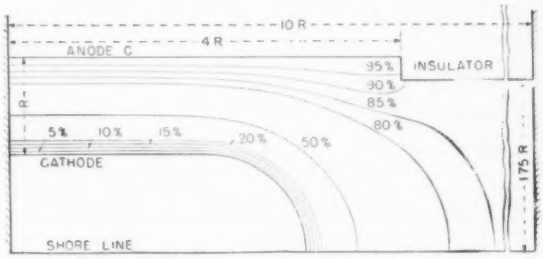

FIG. 4. Potential map, anode *C*

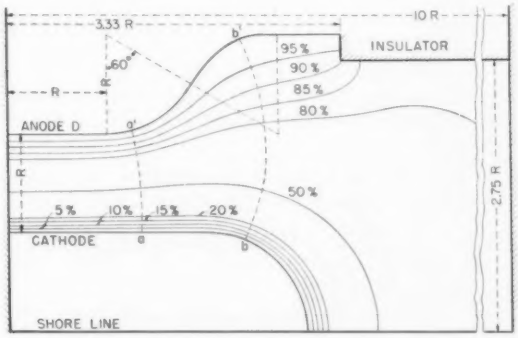

FIG. 5. Potential map, anode *D*

changed to a normal conductance bridge by removing the probe so that the cell comprised only one arm of the bridge. A variable resistance R_p and a parallel variable capacitance C_p were placed in the adjacent arm to balance the bridge. One lead from the detector was connected between these two arms, the other to the center of the potentiometer.

A model of two parallel plates, 110 cm diameter, was set up in the wedge-shaped tank for this study. Representative results are tabulated in chronological order in Table II. If R_s and C_s are the resistance and capacitance of the cell, which in series are equivalent to the parallel combination R_p and C_p, the former can be computed from the measured quantities by the well-known relationships

$$R_s = R_p/1 + (\omega R_p C_p)^2 \qquad \text{(VI)}$$

and

$$C_s = 1/\omega^2 C_p R_p R_s \qquad \text{(VII)}$$

where $\omega = 2\pi$ (frequency). The quantity $(\omega R_p C_p)^2$ was negligible in comparison with unity, so that

TABLE II. *Conductance bridge measurements*

Distance between electrodes, cm	Frequency cycles/sec	Volts across bridge	R_p ohms	C_p μf	C_s μf
90	1000	25	11,100 ± 1	$<10^{-4}$	>200
		2.5	11,100 ± 5	$<10^{-4}$	
		0.25	11,100 ± 25	$<10^{-4}$	
90	3000	25	11,100 ± 1	$<10^{-4}$	
		2.5	11,100 ± 5	$<10^{-4}$	
		0.25	11,100 ± 25	$<10^{-4}$	
90	30	25	11,098 ± 1	5×10^{-4}	
		2.5	11,100 ± 5	5×10^{-4}	
		0.25	11,100 ± 25	5×10^{-4}	
1.25	300	25	155.8 ± 0.1	0.027*	
		2.5	155.8 ± 0.1	0.027	
		0.25	155.8 ± 0.1	0.027	
1.25	1000	25	155.4 ± 0.1	0.0028*	380
		2.5	155.4 ± 0.1	0.0028	
		0.25	155.4 ± 0.1	0.0028	
1.25	100	25	155.1 ± 0.1	0.200*	
		2.5	155.1 ± 0.1	0.200	
		0.25	155.1 ± 0.1	0.200	

* Corrected for the capacitance due to the close proximity of the copper plates, assuming the dielectric constant of the solution to be that of water.

$R_s = R_p$ in all cases. The real electrical analogue of the a-c polarization may comprise a combination of one or more capacitances in series or parallel with one or more resistances, but any such combination may be reduced to the equivalent series combination $C_s - R_s$ for the purpose of this discussion.

Wien (5), Miller (6), Jones and Bollinger (7), and others have demonstrated that a-c polarization adds a resistance, always positive, in series with the true resistance of the electrolyte. The polarization resistance, ΔR, varies with frequency according to the Warburg equation:

$$\Delta R = R_s - R_T = k\omega^{-1/2} \qquad \text{(VIII)}$$

where R_T is the true resistance and k is a constant. The validity of this relationship has been confirmed by Jones and Christian (8) using various electrodes and electrolytes. Thus the series resistance R_s increases as the frequency decreases, the magnitude of this increase being a measure of polarization. The data of Table II do not reveal an increase in R_s on decreasing the frequency, although very small increases would be obscured by the continually decreasing resistance caused by exposure of the electrolyte to room air. The consecutive readings shown in Table II were taken as quickly as possible. They indicate negligible polarization resistance at 1000 cycles/sec. The capacitive component of the a-c polarization is also a negligible effect, the reactance of 380 μf at 1000 cycles/sec being only 0.42 ohm.

It is noteworthy that the procedure used in measuring potential gradients from the equipotential maps avoids errors caused by polarization resistance, when ΔR is relatively small, and by polarization capacitance, even when the latter is a relatively large effect. This is apparent from the vector diagram of the potential mapping bridge, shown in Fig. 6. Here the potential drops are represented by aa' across the potentiometer, ab and $b'a'$ across the

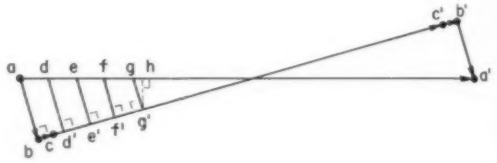

FIG. 6. Vector diagram for the potential mapping bridge

polarization capacitance, bc and $c'b'$ across the polarization resistance, and cc' across the electrolyte. Points d, e, f, and g on the potentiometer cut off 5, 10, 15, and 20 per cent of the total resistance, respectively. The corresponding points d', e', f', and g' in the electrolyte cut off the same percentages of R_s, the combined electrolyte plus polarization resistances. The latter points, sought out by the probe, yield minimum signals when dd', ee', etc., are perpendicular to bb'. If the polarization resistance is negligible, then no error is introduced by the capacitive potentials ab and $b'a'$. If bc is a relatively large fraction of bd', the positions of d', e', f', and g' in the electrolyte will be considerably displaced, but the separations $d'e'$, $e'f'$, and $f'g'$ may be increased very little. Thus our method of omitting b' and using only d', e', f', and g' in determining the slope of the linear curve V vs. $f(r)$ tends to eliminate the effect of polarization resistance.

It should be pointed out that the procedure of fixing the position of the detector on the potentiometer and then moving the probe in the electrolyte to the position of minimum signal may not be reversed without error, if the capacitive polarization

voltage ab is relatively large. Thus point g' in the solution gives minimum signal when the detector is fixed to g on the potentiometer; but if the probe is set at g', the potentiometer slider will seek out position h for minimum signal.

Electrodeposition of Chromium

The distribution of chromium, electrodeposited under common plating conditions, was measured with anode geometries B, C, and D for comparison with the potential gradient distribution. These anodes were accurately machined out of 7 per cent antimony-lead on one tenth the scale used for potential plotting, i.e., $R = 7.5$ mm. The cylindrical cathodes with hemispherical ends were made of copper.

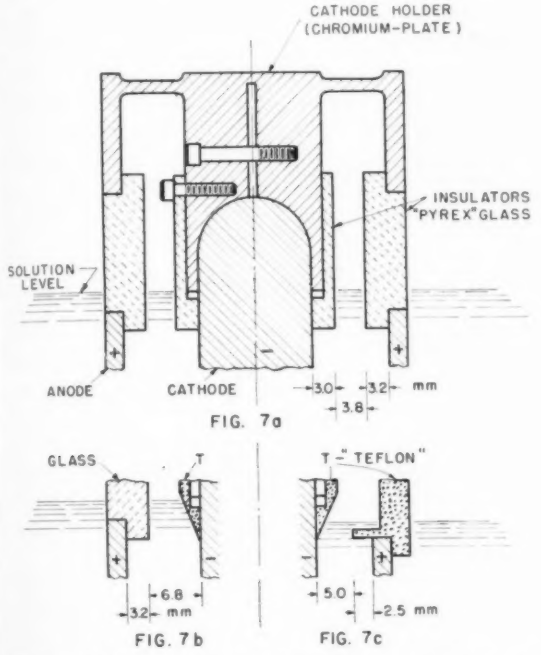

FIG. 7. Cathode holder and insulator arrangement for chromium plating.

Fig. 7 shows the cathode holder and insulators by means of which the electrodes were accurately spaced. The bottom insulator, upon which the anode rested, was made of Pyrex glass or Teflon plastic (polytetrafluoroethylene). The electrode assembly was placed in a wide dish of electrolyte maintained at constant temperature and level. Approximately 40 holes, 4 mm diameter, were drilled in each anode in order to allow diffusion of electrolyte to the cathode from the main body of the solution. The holes were positioned close together in the area of low anode current density (opposite the hemispherical portion of the cathode) in order that any change in anode current distribution be in the direction of greater uniformity.

Chromium deposition was carried out from a bath containing 250 g/l of CrO_3 and 2.5 g/l of H_2SO_4 at 45°C with a mean cathode current density of 15.0 amp/dm^2. A mean thickness of roughly 100 microns was deposited. The plated specimen was cut in a plane containing the axis of symmetry, mounted in bakelite, and polished to 4/0 grade emery paper. The chromium distribution was measured microscopically with an accuracy of ± 2 microns, and duplicate distributions generally agreed within this variation.

The solid curves in Fig. 8 show the measured chromium distributions. Curve a, anode B, was obtained with the insulator arrangement of Fig. 7a.

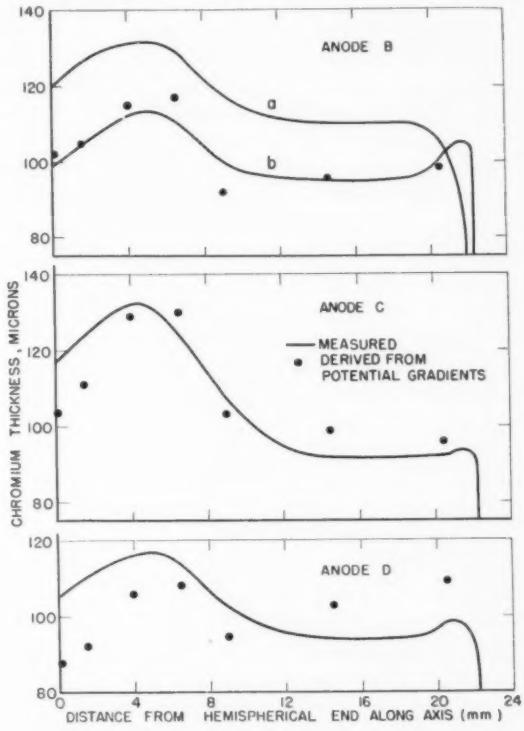

FIG. 8. Distribution of electrodeposited chromium

The sharp reduction in chromium thickness near the top of the cathode was evidently caused by trapping of hydrogen just under the glass insulator surrounding the cathode. Accordingly the latter was replaced by the tapered Teflon insulator shown in Fig. 7b, and curve b of Fig. 8 obtained. With anodes C and D the insulator arrangement of Fig. 7c was used.

The solid points plotted on Fig. 8 represent chromium distributions calculated from the potential gradients of Table I corrected for the variation of cathode current efficiency with current density. If i_L is the local cathode current density and e_L the corresponding current efficiency, then

$$\frac{\text{Local Cr} - \text{thickness}}{\text{Mean Cr} - \text{thickness}} = \frac{i_L e_L}{i_M e_M} \qquad \text{(IX)}$$

where i_M and e_M are the mean values. The local current density was computed from the potential gradients:

$$\frac{i_L}{i_M} = \frac{(dV/dr)_L}{(dV/dr)_M} \qquad (X)$$

The current efficiency data of Dubpernell (9) were used in these calculations.

Discussion

In electroplating applications, which usually involve large d-c polarization voltages that vary with current density, nonuniform current density over either electrode results in deviations from the primary (geometrical) current distribution. Where the cathode current density is relatively uniform but the anode current density varies widely, as for the geometries studied herein, only anode polarization need be considered. Although anode A yields the most uniform cathode current distribution of those studied, its secondary distribution (with polarization) would exhibit the greatest deviation from the primary since A has by far the most variable anode current distribution.

With all four anodes, the cathode current density shows large variations near the junction of the cylindrical to the hemispherical portions. In order to reduce these variations, the anodes would have to be bent closer to the cathode opposite the cylindrical portion, which would make the anode current distribution even less uniform. There is evidently no continuous anode which will yield relatively uniform current distribution over both the selected cathode and itself, where the two electrodes are separated by a distance R or greater.

Furthermore all the anodes studied have shapes that cause the cathode current distribution to become less uniform under conditions of anode polarization. This may be illustrated by the current lines aa' and bb', Fig. 5, drawn to the areas of maximum and minimum anode current density, respectively. Since the polarization voltage will be greater at a' than at b', the cathode current density ratio b/a, which was greater than unity in the primary distribution, will become still greater in the secondary distribution. Any modification of the anode to reduce b/a in the primary distribution increases this polarization effect.

Deviations between the observed and calculated chromium distributions in Fig. 8 may be assumed to result mainly from anode polarization effects. The current density varies most widely over anode D; therefore D should show the greatest deviation due to polarization. Anode B is situated farthest from the cathode and hence should show the least deviation. These considerations conform qualitatively with the distributions in Fig. 8. In addition, the deviations observed with anodes C and D are in the right direction. In the case of anode B, no deviations greater than experimental error are evident. It is possible that part of the observed deviations result from the presence of the gases rising up along each electrode. Since the electrodes are more closely spaced near the top, a relatively larger decrease in current would occur there.

It might be pointed out that the current-distribution problem discussed above is of the following general type: given an equipotential surface over which the potential gradient is uniform (or varies in a stipulated manner), solve for equipotential surfaces outside of it. This kind of problem is an important one which arises frequently in electrodeposition; in practice the minimum metal thickness over an article to be plated is specified as a fixed percentage of the mean, and the other electrode must be designed to accomplish this. The method of designing described herein exemplifies the indirect approach involving successive approximations. Simpler, more direct methods are needed.

Conclusions

1. Copper electrodes in 0.005 per cent potassium dichromate solution may be utilized for potential mapping by the electrolytic trough method with negligible polarization errors.

2. There appears to be no continuous electrode with relatively uniform current distribution over itself as well as over the cylinder with hemispherical ends, where the diameter of the former is at least twice that of the latter.

3. Primary current distributions over the cylinder with hemispherical ends are readily obtainable with maximum deviations from the mean of about 10 per cent. To decrease this deviation, the other electrode must be reshaped in the direction of more variable current distribution over itself.

Acknowledgment

The author is indebted to Dr. J. W. Coltman, Manager of the Electronics and Nuclear Physics Department, and Dr. J. Slepian, Associate Director, of these Laboratories for valuable discussions of this work. Additional credit is due Dr. Coltman for initial work on a-c polarization in the copper-potassium dichromate system.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the Journal.

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Electrodeposition of Germanium[1]

G. Szekely

Physics Laboratories, Sylvania Electric Products Inc., Bayside, New York

ABSTRACT

A process has been developed for electrodepositing a substantial layer of metallic germanium which adheres well. The plating bath is a solution of germanium tetrachloride in propylene glycol. It is conveniently operated at a temperature of 50°–60°C.

Introduction

Germanium, which is about the thirty-sixth (1) most abundant metal in the earth's crust, is obtained in this country as the by-product of a by-product. Consequently, its cost is high—upward of $200 per lb. Most plating operations are carried out at cathode current efficiencies greater than about 50 per cent (chromium at 12–15% being a notable exception). In the case of an expensive metal, however, the use of thin electrodeposited layers in place of thicker layers may effect such large material savings that the costs of deposition, i.e., solution, power, and labor costs, are relatively unimportant. Accordingly, the work described below was undertaken with the viewpoint that conventional solvents, plating speeds, and current efficiencies were not determining factors in guiding the program of investigation.

The discoverer of the element germanium, C. Winkler, electrolyzed ammoniacal ammonium tartrate solutions of the metal and reported a poorly-adhering germanium film on a platinum cathode (2). Dennis and Tressler (3) dissolved germanium dioxide in molten cryolite or potassium fluogermanate and electrolyzed the mixture in graphite crucibles, apparently obtaining pellets of germanium. Hall and Koenig (4) described the electrodeposition of coherent, steel-gray germanium from aqueous potassium hydroxide solutions of germanium dioxide. However, deposition stopped as soon as a thin germanium film covered the cathode completely and only hydrogen was then liberated. They also electrolyzed a molten mixture of potassium and sodium carbonate in which germanium dioxide had been dissolved and obtained crystalline, silver-gray deposits; the platinum cathode used seemed to alloy with the germanium. Schwarz and co-workers (5), using various alkaline and acidic aqueous solutions, confirmed the fact that germanium can be deposited only until a thin film covers the cathode, after which hydrogen is evolved. Their measurements showed the deposition potential of germanium on copper to be lower than that of hydrogen on copper, with the situation becoming reversed when the cathode is electrolytic germanium. However, alkaline oxalate solutions proved to be suitable for quantitative codeposition of germanium and tin. Lloyd and Pugh (6), in England, described a process of separating germanium from the ore, germanite. As part of the process, an alkaline extract of the ore is electrolyzed and a mixed deposit of gallium and germanium obtained.

Fink and Dokras (7) reported the use of a molten salt bath and several organic baths. The salt bath consisted of a molten mixture of borax and germanium dioxide; a graphite rod suspended in the melt served as anode and the graphite crucible as cathode. Molten germanium collected at the bottom of the crucible. The organic baths contained germanium iodide dissolved in glycerine, ethylene glycol, or diethylene glycol and were reported to give deposits of germanium upon electrolyzing.

An attempt was made in these laboratories to adapt the borax bath, for electrowinning germanium, to a plating bath. Silvery, adherent, but brittle films of germanium metal, as much as one mm thick, were deposited on strips of nickel. The disadvantages of this bath are twofold. First, its operating-temperature range includes the melting point of germanium (958°C). At these temperatures metals used as cathodes readily diffuse or dissolve in the bath or the deposit, thus leading to impure germanium. Second, as the cathode is withdrawn from the bath a considerable amount of the melt adheres to it, making it necessary to go through a lengthy operation of dissolving and leaching.

Experiments have shown that at the operating temperatures of the organic germanium iodide bath, 140°–150°C, considerable decomposition as well as solvent loss occurs. A large quantity of other compounds deposits with the germanium, as shown by a white film of nonmetallic appearance which separates out with the steel-gray germanium film. The deposit flakes off easily.

In their discussion of the possibility of plating germanium from nonaqueous solutions, Fink and

[1] Manuscript received January 31, 1951. This paper prepared for delivery before the Washington Meeting, April 8 to 12, 1951.

Dokras eliminated germanium chloride and fluoride because of their volatility, preparative difficulty, and reaction with moisture. However, the germanium tetrachloride baths developed in these laboratories give thick, well-adhering germanium films, metallic in nature, of silvery mirrorlike brightness, and apparently of a high degree of purity. The baths are conveniently operated at 50°–60°C, at which temperature neither decomposition nor appreciable loss of solvent or solute occurs.

Experimental

Many varieties of organic solvents for germanium tetrachloride were tested and two of them, ethylene glycol and propylene glycol, proved suitable for a plating process. Solutions of the chloride in either of these glycols were used as plating baths. To describe the effect of variations of bath conditions upon the process of deposition, two principal kinds of data were collected: the appearance of the deposits and the cathode current efficiency. Bright plating was focused upon for the purpose of arranging the experimental data around a set of conditions at which mechanically sound deposits are obtained.

The ethylene glycol bath worked most successfully with a germanium anode. The germanium anode current efficiency is very large in comparison with the cathode current efficiency. With the ethylene glycol bath, then, knowledge of the bath concentration may be obtained indirectly from the initial concentration and the amount of germanium dissolved anodically as calculated from anode current-efficiency determinations. In the case of the propylene glycol bath a graphite anode may be used, thus allowing operation at essentially constant germanium concentration.

Apparatus

The electrolytic cells used in this work were of two types. For preliminary purposes, a beaker or three-neck organic reaction flask was used in which flat, rectangular cathodes from 1 to 4.5 cm² were plated. Rod-shaped anodes were used, and centrifugal-type glass stirrers agitated the bath when desired. For more precise work, a beaker-type vessel was used containing a cylindrical anode concentric with the cathode assembly (a Lucite shielded rotation shaft holding a cylindrical metal sleeve). The rate of rotation of the cathode could be controlled since the pulley-driven shaft provided three speeds. The latter were determined with a Strobotac. The cathodes[2] were readily dismounted from the shaft by loosening the Lucite tip *T*. The plastic shields as shown in Fig. 1 helped provide an essentially uniform distribution of current density over the entire cathode surface. The whole cell was set into a thermostat-controlled oil bath.

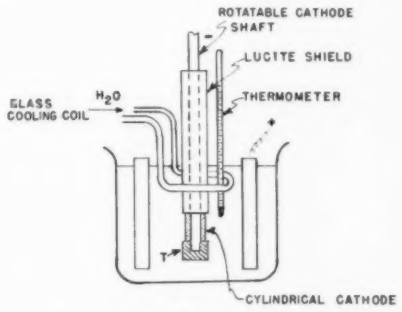

Fig. 1. Constant current density cell

The Germanium Tetrachloride-Ethylene Glycol Bath

Bath composition.—Although germanium tetrachloride is quite soluble in ethylene glycol, the bath concentration must be kept relatively low since mixtures containing about 10 per cent or more germanium tetrachloride precipitate white crystals upon standing. Similarly, the large effect of the germanium anode corrosion has to be taken into consideration; again, a low metal concentration is desired to prevent the separation of a solid phase. Table I shows the effect of concentration upon the behavior of the bath. Above the concentration of 1.0 vol. per cent germanium tetrachloride, plating under the conditions of Table I gives bright metallic deposits of silvery luster. Below 1.0 vol. per cent the deposits become dull, gray, and rough. Around 0.1 vol. per

TABLE I. *Cathode current efficiency and appearance of deposits as a function of concentration in the germanium tetrachloride-ethylene glycol bath*

Initial concentration (Vol. % $GeCl_4$)	Average conc. during 30 min run based upon anode efficiency data (g Ge/100 cm³)	Cathode current efficiency (%) $Ge^{++} + 2\epsilon \rightarrow Ge^0$	Range
3.0	2.06	0.52	Bright plating
3.0		0.54	
1.5	1.11	0.46	
1.5		0.42	
1.0	0.79	0.25	
1.0		0.21	
0.5	0.47	0.18	Nonbright plating
0.5		0.17	

50 ml portions of solution were electrolyzed at a cathode current density of 0.2 amp/cm², a temperature of 50°C, and agitation corresponding to a cathode surface velocity of 11 m/min Ge anode, Cu cathodes.

[2] Dissolution of the copper cathode sleeve in the solution was avoided by having the plating circuit closed by the introduction of the cathode and opened by its withdrawal from the solution.

cent black, smutty deposits are obtained. It will be observed that the cathode current efficiency increases with increasing germanium concentration. The efficiencies were calculated throughout on the basis of a two-electron change (see Table IV).

TABLE II. *Influence of current density and temperature on deposition in the germanium tetrachloride-ethylene glycol bath*

Temperature (°C)	Current density (amp/cm²)	Observations
21–26	0.05	Deposition first observed if cathode is exposed to high agitation
	0.15	First bright film
	0.24	Bright deposition
53–56	0.07	Deposition first observed
	0.11	
	0.15	Bright deposition
	0.20	
	0.30	
78–80	0.05	No deposit
	0.10	Deposition first observed
	0.20	Bright deposits but of coarser grain than at lower temperatures. (The rate of solution of the lacquer used becomes larger at higher temperatures; this indirect effect of temperature may also have been responsible.)
	0.50	

Plating conditions: conc. = 3.8 vol. % $GeCl_4$ throughout. The bath was agitated.

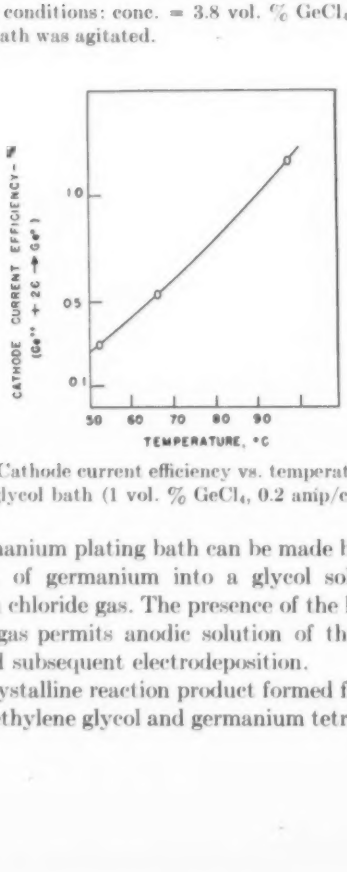

FIG. 2. Cathode current efficiency vs. temperature of the ethylene glycol bath (1 vol. % $GeCl_4$, 0.2 amp/cm²).

A germanium plating bath can be made by anodic corrosion of germanium into a glycol solution of hydrogen chloride gas. The presence of the hydrogen chloride gas permits anodic solution of the germanium and subsequent electrodeposition.

The crystalline reaction product formed from mixtures of ethylene glycol and germanium tetrachloride can also be dissolved in ethylene glycol to provide a bath from which metallic germanium films can be obtained upon electrolysis.

Current density and temperature.—To determine the range of current densities over which germanium deposition takes place, 50 ml portions of solution were electrolyzed. The results for three different temperatures are given in Table II.

It is apparent that bright deposits can be obtained at current densities ranging from about 0.1 amp/cm² upward.

A more quantitative picture of the effect of temperature upon germanium deposition is given in Fig. 2 which shows that an increase in temperature causes a large increase in cathode current efficiency. Experiments showed that the moisture content of the ethylene glycol bath affects the cathode current efficiency considerably. The data presented in Table I and Fig. 2 are self-consistent though only relative, since different batches of glycol were used for the two sets of data.

Agitation.—Agitation was not found to exert a statistically significant effect upon cathode current efficiency over the range of surface speeds from 0 to 30 m/min. However, deposits obtained at 0 m/min were dull while those obtained for surface speeds equal to or greater than 11 m/min (50°C, 1.3 vol. % $GeCl_4$, 0.2 amp/cm²) were bright.

Moisture content of bath and state of solvent.—The effect of the state of purity of ethylene glycol upon the functioning of the bath is indicated by the data in Table III. Electrodeposition was carried out in baths made from C.P. ethylene glycol and from the products of vacuum distillation of this material, the same conditions being maintained in both cases. Determinations of the water content of the glycol were made by means of the Karl Fischer reagent. Throughout this part of the work the moisture content of the germanium tetrachloride was neglected. The same batch of this material was used later for experiments in which the effect of varying moisture content was studied.

Table III shows that vacuum distillation of the solvent permits bright plating at a higher current efficiency; this seems to be associated with two conditions: (*a*) a lower moisture content of the solvent, and (*b*) the absence of what seems to be an organic impurity or perhaps a polymer of ethylene glycol. With respect to moisture content of the solvent, it was found that 20 mg H_2O/cm³ prevent the electrodeposition of germanium (50°C, 1.3 vol. % $GeCl_4$, 0.2 amp/cm², 11 m/min).

Anode current efficiency.—Electrolysis of 50 cm³ of a 1.3 vol. per cent germanium tetrachloride in ethylene glycol solution for 30 min at an anode current

density of 2.8 amp/dm² and a temperature of 50°C yields:

Anode current efficiency
= 57.3% assuming $Ge^0 \rightarrow Ge^{++} + 2\epsilon$ at anode
= 114.6% assuming $Ge^0 \rightarrow Ge^{++++} + 4\epsilon$ at anode.

After correcting for the small amount of germanium which dissolves without application of an external potential difference, during the same time interval and under the same conditions, these values become 56.7 and 113.4 per cent, respectively. It seems, then, that at least some of the germanium dissolves in the divalent state.

Stability of chloride content of bath.—Before and during the progress of electrolysis, 5-ml samples of solution were withdrawn, dissolved in 100 ml of water, and allowed to stand for 64 hr[3]. Volumetric chloride ion determinations were then made and it was found that there was no loss of chloride at 50°C, even after 90 minutes electrolysis at 0.2 amp/cm².

Formation of crystalline substances.—Two types of crystalline materials are formed:

1. When mixtures containing about 10 per cent or more of germanium tetrachloride in ethylene glycol are prepared, large white transparent crystals are formed upon standing. The crystals are soluble in alcohol, acetone, dioxane, and ethylene glycol, but insoluble in ether and germanium tetrachloride. Water decomposes the crystals with the formation of a white powder (assumed to be germanium dioxide) which is soluble in excess water.

Attempts to recrystallize the substance from several solvents failed. However, two extractions with ethyl alcohol followed by three extractions with ether yielded a product which, when dried at 70°C, melted at 102°–104°C. These crystals decompose rapidly in moist air and acid fumes are formed.

Aqueous NaOH added to the crystals yielded a mixture which was distilled. The fraction collected near 200°C reacted with 3,5-dinitrobenzoyl chloride. The product, when washed with aqueous sodium carbonate and recrystallized from alcohol, yielded a derivative which melted at 164.5°–165.5°C. The 3,5-dinitrobenzoate of ethylene glycol, prepared directly, melted at 165°–168°C. A mixed melting point determination using those two substances showed no lowering of the melting point of the mixture (164.5°–165.5°C). These results suggest the presence in the crystals of ethylene glycol or a group easily hydrolyzed to ethylene glycol. The crystals were dissolved in water and volumetric chloride determinations performed. Germanium was determined gravimetrically as germanium dioxide by oxidation of the white germanic sulfide precipitated from a solution of the crystals in water. The results are summarized in Table IV.

An approximate molecular weight determination indicates the molecular weight to be 291 ± 31.

As a result of the above evidence, the formulas $GeCl_2 \cdot (CH_2OH\ CH_2OH)_2$, mol. wt 267.6, and $GeCl_2(OCH_2CH_2OH)_2$, mol. wt 265.6, are submitted as possible alternatives.

TABLE III. *Appearance of deposit and cathode current efficiency as a function of the state of the solvent (germanium tetrachloride-ethylene glycol bath)*

	H_2O content of ethylene glycol (mg/ml)	Appearance of deposit	Cathode current efficiency (%) $Ge^{++} + 2\epsilon \rightarrow Ge^0$
1. Ethylene glycol, C.P., as received (yellow tinge)	1.3	Black, smutty	0.42
2. Same material, vacuum distilled at 90°C. *First fraction* (colorless)	—	Bright, metallic	0.55
3. Same material, vacuum distilled at 90°C. *Second fraction* (colorless)	0.2	Bright, metallic	0.60
4. Distillation residue*	0.3	Slightly dull	0.16

Plating conditions: initial conc. = 1.5 vol. % $GeCl_4$ (corresponding to 0.95 g Ge/100 ml), average conc. during 30 min run = 1.11 g Ge/100 cm³, temp = 50°C, current density = 0.20 amp/cm², cathode surface speed = 11 m/min.

* The yellow tinged glycol became colorless after heating about ½ hour without distilling. During the separation of the second fraction, the residue took on a yellow color which gradually intensified. Upon cooling the residue, a yellow tinged solid separated on the walls of the distillation flask.

TABLE IV. *Results of analyses of reaction product of germanium tetrachloride and ethylene glycol*

	Wt % found	Wt % calculated for $GeCl_2C_4H_{12}O_4$	Wt % calculated for $GeCl_2C_4H_{10}O_4$
Ge	25.9*	27.1	27.1
Cl	26.5	26.5	26.7
C	18.06	18.0	18.1
H	4.24	4.52	3.80

* The procedure used for germanium analysis was found inherently to yield results low by 0.5–1.5%.

[3] The samples removed after 70 and 90 min formed a yellow water solution. This gave unclear endpoints with the Mohr titration and the adsorption indicator methods for determining chloride ion. The yellow color faded on standing about 48 hr with access to air; the Mohr titration then gave a clear endpoint.

2. With time, the germanium concentration in the ethylene glycol bath increased, causing an increase in the cathode current efficiency. If the concentration is not adjusted, a point is reached at which needle-like white crystals precipitate. These crystals give a yellow solution when added to a small amount of water, a behavior similar to that observed when dissolving some of the worked plating solution in water, but different from that of the crystals just described. The melting range of this second type of crystal is considerably above that of the first type. The crystals redissolve when the plating bath is diluted with ethylene glycol and bright plating can be resumed.

The Germanium Tetrachloride-Propylene Glycol Bath

It is clear that electrodepositing germanium from the germanium tetrachloride-ethylene glycol bath represents a considerable improvement over prior methods. The bath deposits uniformly bright metallic germanium films which adhere well to the base metal. No organic or inorganic compounds appear to deposit with the germanium. At the operating temperatures of the bath neither the chloride nor the solvent volatilize to any appreciable extent. However, there are several objections to the bath. A germanium anode makes it impossible to plate at a constant bath concentration; the high anode current efficiency leads eventually to a precipitate which requires diluting the bath to permit further operation. Dividing the current between a platinum and germanium anode is also unsatisfactory since platinum dissolves anodically. Use of a graphite anode appears to interfere with bright plating. Consequently, low initial germanium concentrations are used with a germanium anode, resulting in relatively low rates of deposition.

Many of these difficulties are overcome by the substitution of propylene glycol for ethylene glycol:

1. No solid phase precipitates either when preparing solutions of high germanium content or upon electrolysis of the bath for prolonged periods of time. This permits the use of higher concentrations in the bath with an attendant increase in cathode current efficiency and hence of plating speeds.

2. The rate of water absorption from the atmosphere is smaller for propylene glycol than for ethylene glycol. It is consequently easier to maintain the efficiency of the propylene glycol bath.

3. The bath may be operated with graphite anodes without decreasing the brightness of deposits. This permits operation of the bath at essentially constant germanium concentration.

Temperature, current density, and concentration.—The effect of varying the temperature, current density, and concentration of the propylene glycol bath is seen in Table V. The data represent the results of random experiments of factorial design.

From the columns headed "Appearance of Deposit" in Table V and from an analysis of variance (8) of the efficiency data of the table, the following conclusions are reached:

1. There is a definite trend toward an increase in brightness of the deposits with increasing concentration. The brightest deposits are obtained with solutions containing 7 vol. per cent germanium tetrachloride in propylene glycol. The analysis of variance shows the effect of concentration on the efficiency to be significant (significance level larger than 99%).

2. There may be a slight trend toward brighter plating at the higher temperature. The analysis of variance shows the effect of temperature upon the cathode current efficiency to be significant (significance level larger than 99%). In the case of the two temperatures used, an increase of about 9°C caused an increase of about 18 per cent of the efficiency value at the lower temperature[4].

3. For the 5 and 7 per cent solutions there is a trend at both temperatures for the deposits to become brighter with increasing current density. This is not the case at a concentration of 3 vol. per cent. The analysis of variance for these data shows no effect of current density upon cathode current efficiency.

Previous to designing the experiments summarized in Table V, data were obtained which indicated the existence of a maximum in the effect of germanium concentration upon cathode current efficiency. The experiments of Table V were designed to include, if possible, this maximum range. The analysis of variance bears out the existence of a maximum efficiency between 4 and 7 vol. per cent germanium tetrachloride (temp = 59.3°C, current density = 0.2-0.4 amp/cm²). Using results of additional experiments at 60°C the curve of Fig. 3 was obtained. It is not unreasonable to expect that similar curves, with displaced maximum ranges, would be obtained at different temperatures.

Fig. 3 shows that, as the concentration of germanium in the bath increases above 2 per cent, the cathode current efficiency increases, as would be expected on the basis of a higher rate of germanium repletion of the cathode film.

Somewhere near 5–6 vol. per cent the efficiency begins to decrease with increasing germanium tetra-

[4] A further increase of cathode current efficiency with increase of temperature beyond 59°C may be expected. However, this was not investigated since the Lucite shields used in the constant current density cell (see Fig. 1) are attacked by the bath beyond about 60°C. Solution losses due to volatilization may also be expected at higher temperatures.

chloride concentration. This may be due to an increased rate of hydrogen deposition, due to an increased acidity of the bath, or to the start of a new cathodic reaction.

The data of Table VI indicate that water decreases the rate of germanium deposition from the propylene glycol bath. An increase in water concentration from 0.3 g/l to 1.3 g/l causes an 8.7 per cent reduction in

TABLE V. *Effect of temperature, current density and concentration upon appearance of deposits and cathode current efficiency* ($Ge^{++} + 2\epsilon \rightarrow Ge^{0}$). *Germanium tetrachloride—propylene glycol bath*

Average temp	Vol. % $GeCl_4$	0.2 amp/cm²		0.3 amp /cm²		0.4 amp/cm²	
		Appearance of deposit	Cathode current efficiency (%)	Appearance of deposit	Cathode current efficiency (%)	Appearance of deposit	Cathode current efficiency (%)
50°C	3%	(*a*) Metallic silvery	0.558	Bright with white hue	0.571	Considerable amount of streaking over bright surface	0.524
	5%	Metallic silvery (brighter than *a*)	0.621	Bright with slight streaking over entire surface	0.685	Mirrorlike, minute streaking over surface, some streaking near edges	0.773
	7%	(*b*) Metallic silvery (brighter than *a*)	0.654	Very bright	0.689	Mirrorlike	0.818
59°C	3%	Bright, whitish hue in part	0.750	Bright with good amount of streaking over surface	0.660	Large amount of streaking over entire surface	0.651
	5%	Brighter than *b*, but not mirrorlike	0.868	Almost mirrorlike with slight streaking near edges	0.773	Almost mirrorlike with slight streaking near edges	0.877
	7%	Very bright but not mirrorlike	0.713	Mirrorlike	0.810	Perfect mirror	0.843

Moisture content of propylene glycol = 0.2 mg H_2O/ml
Cathode surface speed = 10 m/min
Graphite anode

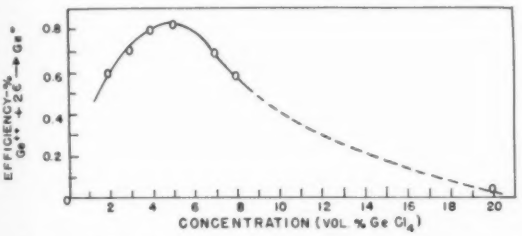

FIG. 3. Cathode current efficiency of propylene glycol bath at 60°C and a current density range of 0.2–0.4 amp/cm².

Moisture content.—The Karl Fischer reagent was used to show that propylene glycol absorbs water from the atmosphere at a lower rate than does ethylene glycol[5].

[5] Equal volumes of the glycols exposing equal surfaces to the atmosphere were left standing in beakers covered with watch glasses. Propylene glycol is more viscous then ethylene glycol and the lower water absorption rate may be due as much to the slower diffusion of absorbed water from the surface as to any intrinsic difference in hygroscopicity.

TABLE VI. *Effect of water content of propylene glycol upon cathode current efficiency*

H_2O content of propylene glycol (mg/ml)	No. of expts.	Average weight gain (mg)	Standard deviation (mg)	Cathode current efficiency (%) $Ge^{++} + 2\epsilon \rightarrow Ge^{0}$	Appearance of deposit
0.3	3	3.24	0.126	0.797	Bright, with a slight amount of streaks
1.3	3	2.96	0.062	0.728	Bright, with a few grey streaks

Plating conditions: conc. = 4 vol. % $GeCl_4$, temp = 60°C, current density = 0.3 amp/cm², cathode surface speed = 11 m/min

cathode current efficiency. (The difference between the two efficiency means is significant at the 95% level.)

Other facts regarding the propylene glycol bath.—At the optimum conditions for bright plating (7 vol. % solution, 59°C, 0.4 amp/cm²; see Table V), germanium deposits at the rate of 0.001 in./3.0 hr (0.025 mm/3.0 hr). The deposit is still bright at a thickness of 0.005 in. (0.127 mm). Analysis of the gas evolved at the cathode showed that it was mainly hydrogen.

A plating bath can be prepared by anodically corroding germanium in a solution of hydrogen chloride gas in propylene glycol. When a germanium anode is used in the bath (temp = 60°C, conc. = 4 vol. % germanium tetrachloride, anode current density = 2.7 amp/dm²), the anode current efficiency is found to be about 58 per cent, assuming the reaction $Ge^0 \rightarrow Ge^{++} + 2\epsilon$.

It was stated above that no solid reaction product was observed as a result of preparing solutions of germanium tetrachloride in propylene glycol. Furthermore, no solid phase precipitates during operation of the bath. However, when using a germanium anode a small amount of a white film may form on it upon prolonged electrolysis. The addition of water to the white solid caused it to turn yellow. The supernatant solution resulting from this gave a white precipitate with silver nitrate solution. This white precipitate turned first reddish, then purple, then brown within a few seconds after its formation.

Summary

An ethylene glycol bath yields adherent bright metallic germanium deposits but shows some difficulty in operation, i.e., the high corrosion rate of the germanium anode and the eventual precipitation of a white crystalline substance resulting therefrom. A propylene glycol bath gives deposits similar to those from the ethylene glycol bath, but shows none of the difficulties of operation inherent in the latter bath.

The optimum conditions for bright plating were shown to be:

Concentration	= 7 vol. % $GeCl_4$ in propylene glycol
Temperature	= 59°C
Cathode current density	= 0.4 amp/cm²
Cathode surface speed	= 10 m/min
Anode	= graphite

At these conditions the plating speed is 0.001 in./3.0 hr (0.025 mm/3.0 hr). Bright germanium can be deposited from the propylene glycol bath to a thickness of at least 0.005 in. (0.127 mm).

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the Journal.

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Functions and Behavior of the Components of Expanders for the Negative Plates of Lead-Acid Storage Batteries[1]

A. C. Zachlin

Development Laboratory, Willard Storage Battery Company, Cleveland, Ohio

ABSTRACT

The effect of various expander components depends on the proportion used and in some cases on the brand chosen. Cold capacity on initial cycles is affected most by lignin, increasing with the proportion of lignin up to 0.5 per cent but not beyond that. Barium sulfate and lamp black affect initial capacity to a lesser degree, but improve the cold capacity and length of service during cycling life. All three components affect the structure of plate surface during the cycling life test. Charge voltage is affected by the concentration of each of the components of the expander.

Introduction

The literature on expanders for the negative plate of the lead-acid storage battery has been reviewed very thoroughly only recently. Ritchie (1) summarized it in an extensive bibliography according to the use and nature of materials used as expanders. Willihnganz (2) discussed the behavior and theory of expander action.

This paper presents the effect of components of compound expanders in various concentrations on the performance of fresh batteries, on their behavior during a cycling life test, and on the appearance of negative plates in batteries that have been worn out to exhaustion.

The approach adopted here for studying the problem of function of expander components was different from that used by Willihnganz. Instead of observing the result of adding to the active material the various components of compound expanders one by one in increasing proportions, observations were made on the result of leaving out the several components individually and reintroducing them at first in small proportions, then in regular proportion, and finally in excess. If Willihnganz's method was synthetic, then this was analytical.

The results of this procedure were measured on initial capacity cycles, on the SAE cycling life test (3), on cold capacity during this life test, and by appearance of the negative active material at the end of the life test.

Ritchie (1) listed the usual concentrations of various expander components as shown in Table I. This table also includes the concentrations studied in this work.

In most cases, the mixes, consisting of 100-lb leady oxide (68% PbO, 32% Pb), expander in dry form, uniform amounts of water, and sulfuric acid, were made in a small dough-type mixer, and then pasted on a Gas Dry machine (4, 5) into grids from a selected uniform lot. The exceptions were the mixes made to production size (over 2000 lb) which provided plates with expanders C, L, and M. The proportions of expander ingredients shown are expressed as percentage ratios of expander ingredient to the weight of oxide used. Table II lists the make-up of expanders studied, gives densities of pastes and weights per single negative plate, and identifies the compositions used by letter symbol.

TABLE I. *Ranges of expander components*

Component	Quoted by Ritchie	Proportions studied in this paper
Lignin	0.05–1.0%	0, 0.3, 0.5, 0.7, 1.0%
Barium Sulfate	0.3%–3%	0, 0.3, 0.6, 1.0%
Lamp Black	0.05–.30%	0, 0.15, 0.5, 1.0%

TABLE II. *Composition of expanders studied and paste properties*

No.	Lignin	Barium sulfate	Lamp black	Wet paste density	Weight of dry paste
	%	%	%	g/in³	lb per plate
A	0	0.3	0.15	66.5	0.217
B	0.3	0.3	0.15	65.8	0.215
C	0.5	0.3	0.15	67	0.226
D	0.7	0.3	0.15	66	0.213
E	1.0	0.3	0.15	65.5	0.219
F	0.5	0	0.15	66	0.227
G	0.5	0.6	0.15	66	0.225
H	0.5	1.0	0.15	65.8	0.224
I	0.5	0.3	0	66	0.220
J	0.5	0.3	0.5	65	0.220
K	0.5	0.3	1.0	64	0.218
L	0.5	0.3	0.15	66.5	0.219
M	0.5	0.3	0.15	69.5	0.243

[1] Manuscript received July 7, 1950. This paper prepared for delivery before the Buffalo Meeting, October 11 to 13, 1950.

The difference between expanders C, L, and M lay in the kind of lignin used, C being a by-product of paper pulp manufacture from hard woods[2], L being a product of treating oak sawdust with sulfuric acid (6), and M being a by-product of paper pulp manufacture from pine wood[3]. Plates with expander C all came from one large mix and were built into duplicate batteries included in each group of expanders.

The positive grids were 0.078 in. (1.98 mm) thick and the negative grids were 0.068 in. (1.73 mm) thick. Both the positive and the negative plates were $4\frac{7}{8}$ in. (123.8 mm) high and $5\frac{11}{16}$ in. (144.6 mm) wide. The positive plates used in these experiments came from one lot, and, therefore, were all similar. The groups of 7 positive plates and 8 negative plates insulated with microporous rubber separators making elements of nominal 100 amp-hr capacity were assembled in hard rubber containers of uniform size

TABLE III

Cycle	Kind of discharge	Capacity measured in
1	5-hr rate to 1.70 v	hr
2	300 amp at 0°F (−17.8°C)	min
3	5-amp rate to 1.75 v at 80°F (26.7°C)	amp-hr
4	300 amp at 0°F (−17.8°C)	min
5	5-amp rate to 1.75 v at 80°F (26.7°C)	amp-hr
6	300 amp at −10°F (−23.3°C)	min
7	5-amp rate to 1.75 v at 80°F (26.7°C)	amp-hr
8	300 amp at −40°F (−40°C)	min

which were then available for these experiments. The cells were filled with sulfuric acid of 1.115 sp gr, formed at a constant temperature of 100° ± 5°F (38° ± 2°C) at the 8.4-amp rate for 28 hr, given a 2-hr rest, formed for 13 hr more at the same rate, and then dumped. The acid was replaced with fresh acid of 1.340 sp gr. The batteries were given a mixing charge at 5 amp overnight and finished with a sp gr of 1.285 ± 0.002. They were given one conditioning discharge at the 5-hr rate, following which they were subjected to the rest of the initial capacity cycles shown in Table III.

Cycles 7 and 8 were run only on batteries with varying concentration of lignin.

The recharges after the cold tests were performed on the bench in the open; those after the 20-hr (5 amp) discharges were conducted at the constant temperature at which the batteries had been formed (7). Following the initial capacity cycles the batteries were placed on the SAE cycling life test (3), Fig. 3, 7, 11, and 14.

At the expiration of a battery test the cells were opened and plates inspected for the cause of failure. Except in the case of batteries which were completely deficient in lignin or barium sulfate in the expander, the life of batteries on this test was terminated by the shedding of the positive active material. Samples of negative plates from each pair of duplicate batteries were washed acid-free in water, then dehydrated in alcohol, and finally dried in an oven.

Selected areas of the surfaces regarded as the most representative of the lot were photographed. The negatives were enlarged to provide prints of uniform 10× magnification shown in Fig. 4, 8, and 12. The individuals of pairs of batteries represented by the photomicrographs were not necessarily the same as the ones which are represented in the graphs.

Results and Discussion

No trend with increasing concentration of the various expander ingredients, nor with different grades of lignin, was observed on the 20-hr capacity. All batteries ran in the neighborhood of 94 amp-hr. This is probably the result of restricted volume of acid in the container used. Cold capacities are not believed to be influenced by this factor within variations involved here. Similarly, no dependence of the 5-sec voltage (3) on concentration of the various ingredients or on grade of lignin appears to exist.

Lignin

Cold capacity.—The cold capacity of a battery on initial cycles on the 300-amp discharge is directly dependent on the proportion of lignin in the negative active material up to 0.5 per cent lignin (Fig. 1). The cold capacity of a battery without lignin is very low, being less than half that of a battery fortified with it to the optimum proportion (0.5%). Although not sufficient, 0.3 per cent lignin helps.

Essentially the same result is obtained when this relationship is measured at the 300-amp rate whether at 0°, −10°, or −40°F (−17.8°, −22.3°, or −40°C), although the effect of proportion at −40°F is less pronounced than at higher temperatures.

Cold capacity during cycling life.—Periodically during the SAE cycling life test (3) the batteries were submitted to a discharge of 300 amp at 0°F (Fig. 2, 6, 10, and 13). This provided an indication of the ability of a battery to maintain its performance in the cold or on cold starting service. The results on lignin are presented in Fig. 2. The futility of trying to make a battery deliver power at cold temperature without the use of lignin is brought out in this graph very sharply. Such a battery is deficient in power from the start, and loses whatever it has within a

[2] "Meadol," Research and Development Department, The Mead Corporation, Chillicothe, Ohio.

[3] "Indulin," Bulletin L-5, Development Department, Industrial Chemical Sales, 230 Park Avenue, New York (1948).

short time. A battery with 0.3 per cent lignin does much better. Batteries with still higher proportions of lignin do still better, but do not differ markedly whether the proportion is 0.5 per cent or twice that.

Cycling life.—The cycling life of a battery is determined normally by the life of positive plates.

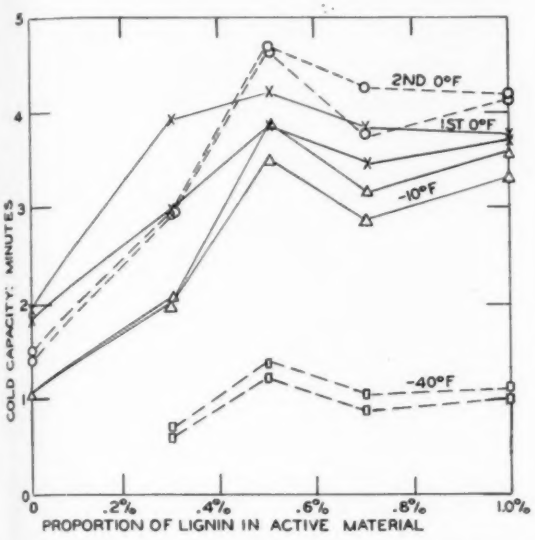

FIG. 1. Effect of proportion of lignin on initial cold capacity.

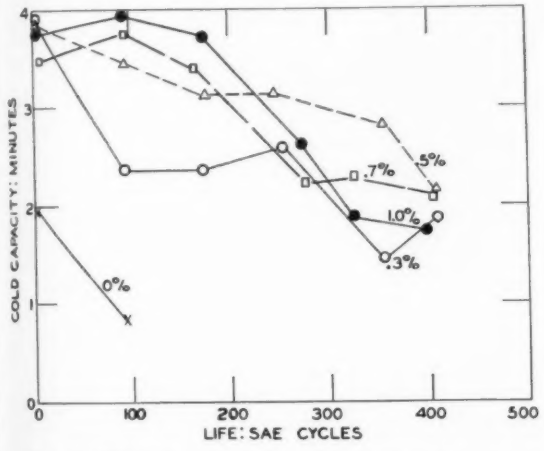

FIG. 2. Effect of proportion of lignin on cold capacity during SAE life test.

When these have shed a certain proportion of their active material the capacity of the battery drops and the test is discontinued when the capacity reaches a predetermined low value. When, however, the negative active material is not provided with the proper expander, then the cycling life of the battery may be cut short by the negative plates before the positives are worn out.

Such was the case with the battery which had no lignin, as Fig. 3 shows. This battery had expander A in the negative active material, that is, it included barium sulfate and lamp black, but not lignin. The result is very striking. Batteries with lignin delivered

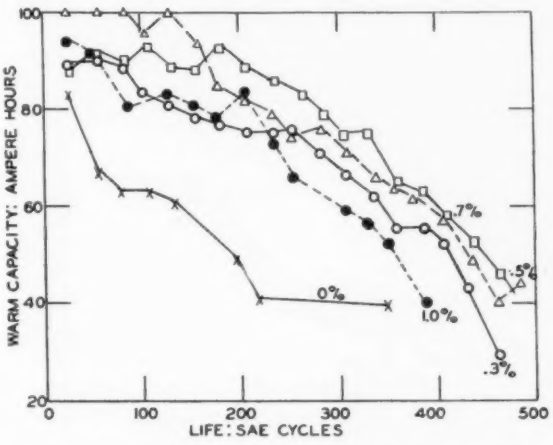

FIG. 3. Effect of proportion of lignin on warm capacity during SAE life test.

TABLE IV. *Variation of negative cadmium voltage during charging of batteries with various proportions of expander ingredients in negative active material*

Proportion of lignin, %	Negative cadmium charge voltage
0	−0.03 v
0.3	−0.16 v
0.5	−0.22 v
0.7	−0.20 v
1.0	−0.22 v
Proportion of barium sulfate, %	
0	−0.14 v
0.3	−0.22 v
0.6	−0.21 v
1.0	−0.20 v
Proportion of lamp black, %	
0	−0.22 v
0.15	−0.22 v
0.5	−0.21 v
1.0	−0.16 v
Kind of lignin	
C	−0.18 v
L	−0.02 v
M	−0.14 v

much higher capacity during the life test and lasted more cycles. There appears to be little difference between the proportions of lignin over the range studied here.

Charge voltage.—Charge voltage of batteries was measured while they were being overcharged at 5

amp between 90° and 100°F (32.2° and 37.8°C). The measurement is best shown as the voltage of the negative plate against a cadmium stick connected

crease beyond 0.5 per cent lignin is practically n
Such a difference on an SLI[4] battery amounts to
volt. This relationship is presented in Table IV.

FIG. 4a. No lignin, 247 cycles

FIG. 4b. 0.3% lignin, 461 cycles

FIG. 4c. 0.5% lignin, 513 cycles

FIG. 4d. 1% lignin, 465 cycles

FIG. 4. Effect of proportion of lignin on the structure of the surface of plates at the end of SAE life test

to a high resistance voltmeter (8). It shows a definite relationship, the voltage being nearly 0.2 volt per cell higher for batteries with optimum proportion of lignin than for those without any, and again the in-

Appearance of plates.—Perhaps one of the most striking distinctions among batteries with and without lignin is shown in Fig. 4. Power available from

[4] SLI = Starting, lighting, ignition automobile battery.

ilgative plates, such as that shown in Fig. 4*a*, is very limited. Batteries with negative plates in condition shown here were discontinued on the cycling life test because of inability of the negatives to deliver power. The positives were still in good condition.

The situation is improved with 0.3 per cent lignin (Fig. 4*b*) but is still not satisfactory. The appearance of a satisfactory negative is illustrated in Fig. 4*c*. Fig. 4*d* showing an active material with 1 per cent lignin looks somewhat different from Fig. 4*c*, but the performance of the two plates was the same. A photomicrograph of the plate with 0.7 per cent lignin was similar to Fig. 4*c* and 4*d*.

Barium Sulfate

Cold capacity.—The dependence of cold capacity of batteries on the content of barium sulfate in the negative active material is not nearly so critical as it

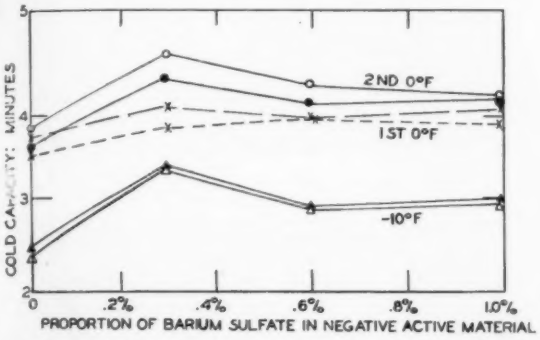

FIG. 5. Effect of proportion of barium sulfate on initial cold capacity.

is on lignin. There is a slight improvement in cold capacity on initial cycles which cannot be overlooked. The decline in capacity with a temperature drop from 0° to −10°F seems to be sharper here than was the case with lignin batteries. On initial cycles, it makes little difference whether the expander contains 0.3 or 1 per cent barium sulfate. The data are shown in Fig. 5.

Cold capacity during cycling life.—Cold capacity during cycling life (Fig. 6) suffers seriously from the omission of barium sulfate from the expander. Its addition to the expander results in better capacity and longer life. The extent of improvement with different proportions cannot be stated precisely although it definitely exists.

Cycling life.—A complete omission of barium sulfate from the expander results in reduced capacity of batteries at ordinary temperatures during their cycling life and in premature failure to deliver power (Fig. 7). Batteries from which barium sulfate was excluded failed because of the negative plates even before the positive plates were worn out. The introduction of this salt produced an increase in cycling life amounting to 50–150 cycles.

Charge voltage.—There is an increase in charge voltage of negative plates with increasing proportion of barium sulfate, although the range covered is not so wide as it was with lignin batteries (Table IV).

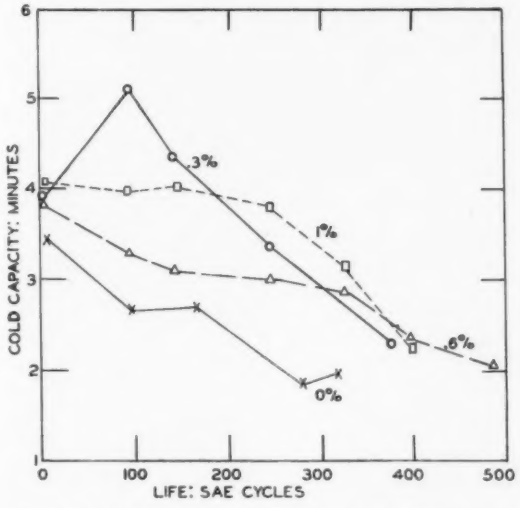

FIG. 6. Effect of proportion of barium sulfate on cold capacity during SAE life test.

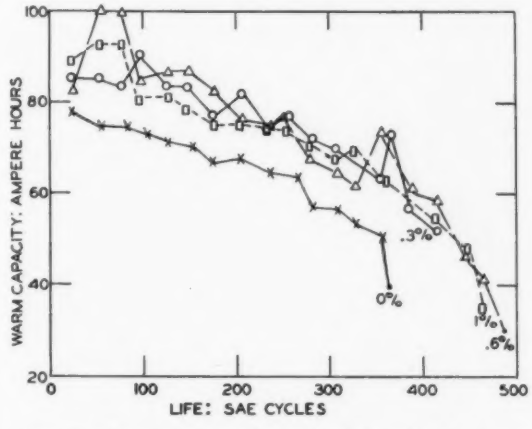

FIG. 7. Effect of proportion of barium sulfate on warm capacity during SAE life test.

Appearance of plates.—The surface of negative active material without barium sulfate (Fig. 8*a*) appears to be more or less lumpy. Apparently the active material was restricted in its expansion by the separators because a number of curving ridges can be seen to have flat surfaces as if the active material had expanded as far as the separator would permit. The inclusion of 0.3 per cent barium sulfate (Fig. 8*b*) decidedly refined the surface of the active material. Doubling of this amount changed the situation

somewhat (Fig. 8*c*) but an increase of its proportion to 1 per cent (Fig. 8*d*) did not gain much advantage. Here again restricted growth is in evidence, except that the surface has a finer structure than where barium sulfate is omitted.

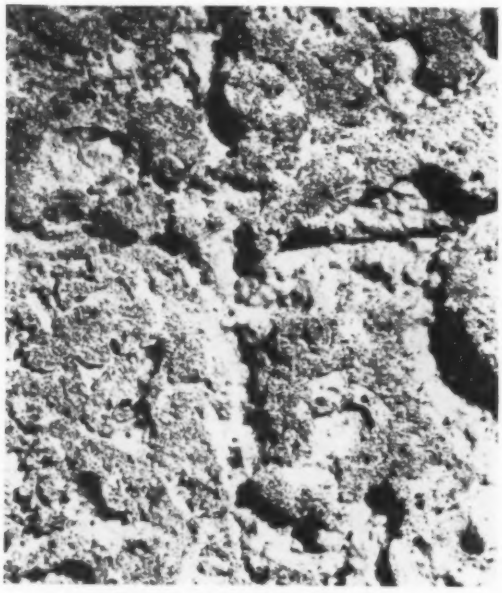

FIG. 8*a*. No $BaSO_4$, 355 cycles

FIG. 8*b*. 0.3% $BaSO_4$, 379 cycles

FIG. 8*c*. 0.6% $BaSO_4$, 489 cycles

FIG. 8*d*. 1% $BaSO_4$, 469 cycles

FIG. 8. Effect of proportion of barium sulfate on the structure of the surface of plates at the end of the SAE life test

Lamp Black

Cold capacity.—Lamp black in the expander is not commonly regarded as a source of improvement in the cold capacity of batteries. It is used mainly, as Ritchie (1) points out, to improve the clearing of the negative plates on formation. For the sake of completeness, however, lamp black was included in this study of expander ingredients. It was evaluated for effect on cold capacity, and was found to exert appreciable beneficial influence (Fig. 9).

Cold capacity during cycling life test.—The addition of a small amount (0.15%) of lamp black seems to

make an appreciable difference in the cold capacity of batteries during the cycling life test; in some cases the effect appears to amount to a whole minute in three (Fig. 10). Strangely, however, greater concentration of lamp black does less good in this sense than the small addition.

Cycling life.—Lamp black up to 1 per cent in negative active material seems to make little difference in the capacity of batteries during the SAE cycling life test or in the length of cycle life (Fig. 11).

Charge voltage.—The trend of effect of lamp black on charge voltage with its increasing concentration evidently is in reverse direction from that of lignin and barium sulfate (Table IV). While the lowest values of charge voltage were met in the absence of the other two ingredients, and the highest values with their highest concentration, in the case of lamp black the highest charge voltage occurs in the absence of lamp black (but presence of lignin and

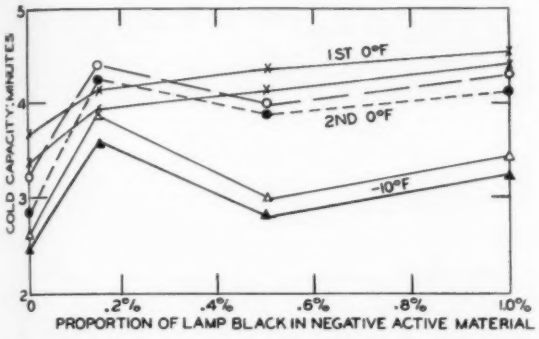

FIG. 9. Effect of proportion of lamp black on initial cold capacity.

barium sulfate) and the lowest value with its highest concentration. Undoubtedly lamp black acts as a depolarizer (9) here, lowering the overvoltage characteristic of the lead electrode.

Appearance of plates.—The surface of negative active material containing lignin and barium sulfate but not lamp black appears to be solid rather than granular, and scattered with unreduced lead sulfate (Fig. 12*a*). The addition of a mere 0.15 per cent lamp black makes a great difference in the structure of the surface causing it to take on a granular appearance with no more than occasional grains of unreduced sulfate (Fig. 12*b*). Further increases in the proportion of lamp black do not refine the surface further and cause little more than clearing (Fig. 12*c* and 12 *d*).

Kinds of Lignin and Other Components of Expanders

At various times the behavior of expander ingredients derived from different sources was studied. For example, it was found that particle size, manufacturing process, and per cent of carbon in lamp black do not noticeably affect the performance of this expander ingredient in the battery. Barium sulfate from some sources caused cracking of negative active material while that from other sources gave good results. This seemed to be related to the particle size and shape of the barium sulfate crystals (10).

The greatest difference in the behavior of expanders seems to be encountered with different kinds of lignin, described above. The comparisons shown here are of value only to the extent that the data are

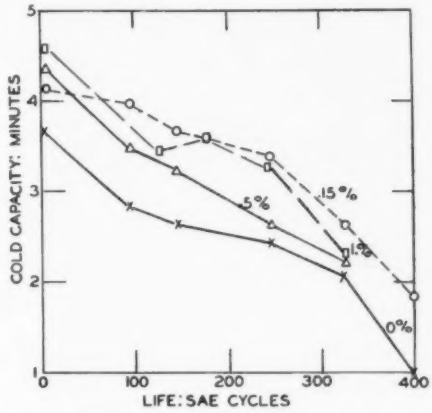

FIG. 10. Effect of proportion of lamp black on cold capacity during SAE life test.

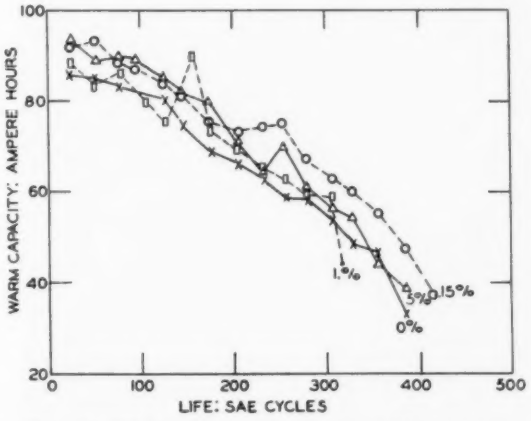

FIG. 11. Effect of proportion of lamp black on warm capacity during SAE life test.

based on experiments performed with painstaking care. Their strength and reliability lie in the fact that each point represents the average of five or six readings. Unfortunately, the length of this experiment made it impossible to repeat it.

Initial cold capacity.—There is little difference in the initial cold capacity of the batteries with the three different lignins studied. Their cold capacity fell within about a half minute of each other (Table V).

Cold capacity during cycling life.—There was a very great difference among the lignins of the three sources

as shown in Fig. 13. Here lignin L is at the bottom. It was the shortest-lived material on warm cycle

FIG. 12*a*. No lamp black, 383 cycles

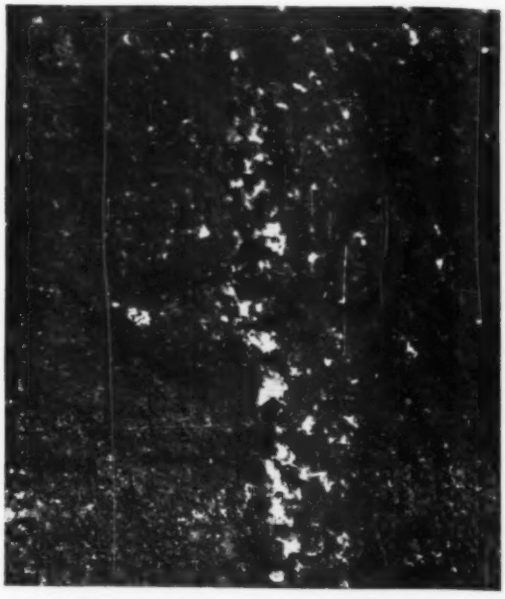

FIG. 12*b*. 0.15% lamp black, 413 cycles

FIG. 12*c*. 0.5% lamp black, 279 cycles

FIG. 12*d*. 1% lamp black, 307 cycles

FIG. 12. Effect of proportion of lamp black on the structure of surface of plates at the end of SAE life test

measurements. Lignin M is outstandingly superior to the other two.

Cycling life.—There is little difference in the warm capacity of these batteries during cycling life (Fig. 14). The length of life was appreciably lower for lignin L than for the other two. This, however, may have been due to some irregularity of the positive plates.

Charge voltage.—There is an interesting difference among the lignins on the charge voltage comparison

(Table IV). Lignin L shows the lowest charge voltage and lignin C the highest.

TABLE V. *Effect of type of lignin on capacity*

Cycle*:	5 hr	0°F	20 hr	0°F	20 hr	−10°F
Capacity*:	hr	min	amp-hr	min	amp-hr	min
Lignin L	5.05	4.42	95.0	4.52	97.1	3.44
Lignin C	4.85	3.98	94.4	4.37	96.1	3.53
Lignin M	5.00	4.56	94.4	4.92	96.4	3.73

* See Table III.

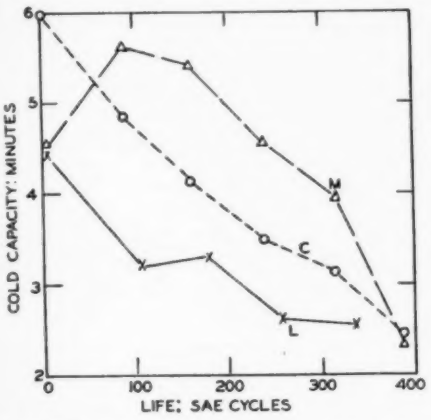

FIG. 13. Effect of brand of lignin on cold capacity during SAE life test.

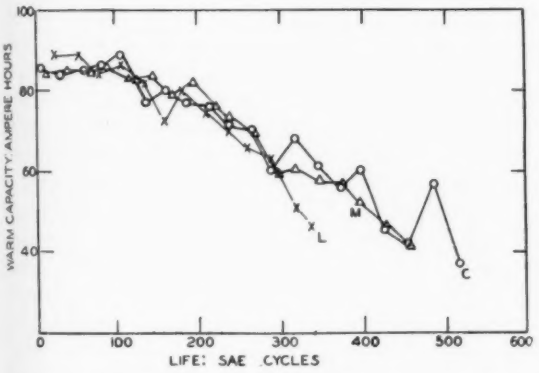

FIG. 14. Effect of brand of lignin on warm capacity during SAE life test.

Appearance of plates.—There was no striking difference in appearance of the surface produced by the three kinds of lignin after a long test service duty.

CONCLUSIONS

The proportion of lignin in the expander exerts a great influence on the initial cold capacity of batteries, improving it increasingly when present in concentrations of up to 0.5 per cent but not further above that. It improves the cycling life and cold capacity during life. Charge voltage is increased with increasing proportion of lignin up to 0.5 per cent. Lignin refines the structure of the surface of the negative plates.

The proportion of barium sulfate has less influence on the performance of batteries than lignin, but is still very effective in cold capacity during life and on length of cycling life. It affects the condition of plate surface very considerably.

Lamp black, which is not commonly regarded as having influence on cold capacity, improves it over cycling life. It also affects the structure of plate surface.

The effect of lignin on cold capacity during life and on charge voltage differs considerably with the kind of lignin used.

Charge voltage is increased with increasing proportion of lignin and barium sulfate, but decreased when the proportion of lamp black is increased.

ACKNOWLEDGMENT

The author takes pleasure in expressing his appreciation to the management of Willard Storage Battery Company for permission to publish this article.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the JOURNAL.

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A Proposed Mechanism for the Discharge of the Manganese Dioxide Electrode[1,2]

D. Thomas Ferrell, Jr., and W. C. Vosburgh

Duke University, Durham, North Carolina

ABSTRACT

Manganese dioxide electrodes prepared by electrolytic deposition on graphite rods were found reproducible in discharge characteristics, though variable in magnitude and constancy of electrode potential. The polarization and recovery from polarization in several electrolytes were studied and many complete discharges were made with measurement of the capacities. A theory of the discharge mechanism is proposed on the basis of the experiments. This is based on the formation of a lower oxide at the inner surface of the manganese dioxide layer on discharge, and the diffusion of this oxide, or oxyhydroxide, into the interior of the dioxide layer. The accumulation of lower oxide during discharge accounts for much of the polarization, and the slowness of its diffusion away through the solid phase accounts for the slowness of the recovery process. Dilution of the manganese dioxide by lower oxide accounts for most of the decrease in the open circuit electrode potential during discharge.

Introduction

The mechanism of the manganese dioxide electrode of the Leclanché cell is not sufficiently well known. The electrode reaction is generally considered to involve production of ammonia, or other basic material, and a lower oxide of manganese. The dependence of the electrode potential on the *p*H of the electrolyte is in agreement with the assumption of a basic product (1–4). The lower oxide has usually been assumed to be an oxide of trivalent manganese, often written as Mn_2O_3 (5–7). McMurdie, Craig, and Vinal (4) identified manganese oxyhydroxide, MnOOH (8), as a product of the reduction of manganese dioxide by manganese(II) ion in the absence of zinc ion, and hetaerolyte, $ZnO \cdot Mn_2O_3$, when zinc ion was present. Copeland and Griffith (9) found hetaerolyte to be a product of the discharge of dry cells. They also found that manganese oxyhydroxide in a bobbin was reducible and would give a discharge, whereas trimanganese tetroxide (Mn_3O_4) and hetaerolyte would not. They considered hetaerolyte formation unfavorable for a maximum discharge. Griffith (10) observed that hetaerolyte is not formed immediately on reduction of manganese dioxide, but in a secondary reaction.

Dry cells show considerable polarization attributable to changes at the manganese dioxide electrode (5, 7, 11) and a larger change in electromotive force on discharge than can be accounted for by change of *p*H or zinc ion concentration, or change in resistance (7, 12). Wadsley and Walkley (13) found that the electrode potential of the manganese dioxide electrode in acid solution containing manganese(II) ion decreased as the oxygen content of the manganese dioxide decreased. If this relationship continues over a wider range of compositions than included in the experiments of Wadsley and Walkley, it can explain at least part of the decrease in electromotive force of the dry cell on discharge. Feitnecht and Marti (14) have prepared a series of manganese oxides or oxyhydroxides in which the ratio of oxygen to manganese, x in the formula MnO_x, varied from 1.11 to 1.95. These compounds were grouped in a limited number of crystal forms, each form including a range of compositions. It was suggested that the oxidation of manganese hydroxide can be considered to take place by removal of electrons from manganese ions and protons from hydroxyl groups, with little change in structure. A similar process can be assumed for the reduction of manganese dioxide (8, 15). These observations are in agreement with the assumption of Keller (7) that solid solution formation between manganese dioxide and a lower oxide is responsible for part of the decrease in the dry cell electromotive force on discharge.

Keller (7) has shown that the manganese dioxide must be in contact with the carbon of the electrode to be effective, the carbon black mixed with the manganese dioxide being a part of the carbon electrode (1, 16). This is not in accord with a mechanism involving the passage of tetravalent manganese in any form through the solution, as Drotschmann has pointed out (17).

[1] Manuscript received July 27, 1950. This paper prepared for delivery before the Buffalo Meeting, October 11 to 13, 1950.

[2] Thesis submitted by D. Thomas Ferrell, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University. This work was carried out under Contract N6ori-107 with the Office of Naval Research.

Coleman (11) considers that a diffusion process within the solid manganese dioxide plays an important part in the temporary polarization phenomena of dry cells. While he does not need to assume a specific process, he suggests as an illustration the formation of manganese oxyhydroxide, MnOOH, on the surface of the manganese dioxide and diffusion inward. As suggested above, such a diffusion could take place by movement of electrons and protons only, the result being the replacement of manganese (IV) ion in the interior by manganese(III) ion and oxide ion by hydroxide.

The object of this investigation was to obtain more data on the polarization and discharge of the manganese dioxide electrode. On the basis of the results obtained with an electrolytic manganese dioxide it has been possible to formulate a more detailed theory of these processes than has been possible previously.

Experimental

Manganese dioxide electrodes were prepared electrolytically. Graphite rods six inches long and three-sixteenths inch in diameter, made for spectrographic analysis, were mounted in short lengths of Pyrex tubing by sealing with glyptal resin at one end of the glass. At the sealed end 5.2 cm of the rod projected beyond the seal, and at the other end, used for electrical contact, about 1.5 cm projected beyond the glass, as shown in Fig. 1. Manganese dioxide was deposited electrolytically from a solution containing 50 grams of manganese sulfate and 67 grams of sulfuric acid per liter at a temperature above 75° C, usually about 90° C (18). The current density was 3.13 ma/cm^2, or 25 ma for the 8 cm^2 of apparent surface area. The time of electrodeposition varied from 15 minutes to four hours, but was carefully controlled so that the relative thickness of the deposit can be stated in terms of the time. The deposit was formed as a tightly adherent coating that was somewhat variable in appearance.

Available oxygen and total manganese determinations were made on some typical electrodes by the arsenious oxide method described by Kolthoff and Sandell (19) and the method of Lingane and Karplus (20), respectively. For electrodes plated for 1 hour at 25 ma, the available oxygen was 0.834 and 0.829 milliequivalent, after correction for 0.009 milliequivalent found for a graphite rod at which oxygen had been evolved for an hour. The total manganese in two other electrodes was 0.416 and 0.416 millimoles. For electrodes plated 30 minutes the available oxygen was 0.435 and 0.430 milliequivalents, and the total manganese 0.209 and 0.207 millimoles. The material on the electrodes can be considered to be manganese dioxide within the limit of error of the method. The current efficiency was 89 per cent.

The plated portions of a number of these electrodes were immersed in buffered salt solutions, and the electrode potentials measured against a reference electrode of silver and silver chloride in 1*M* potassium chloride solution. Electrode potentials referred to this electrode can be converted to potentials referred to the zinc electrode by the addition of one volt. The manganese dioxide electrodes were not very reproducible in electromotive force, and their constancy depended on the nature of the electrolyte. With ammonium chloride and ammonium sulfate electrolytes, buffered by a small concentration of ammonia, the electrode potential decreased slowly for as much as two months. The changes on standing in a solution are being studied further.

In spite of the inferior reproducibility in electrode potential and the lack of constancy, the discharge characteristics of the electrolytic electrodes were quite reproducible. It was possible to study the discharge without serious errors from either of the defects.

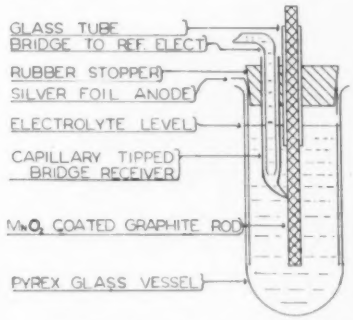

Fig. 1. Cell used for discharge experiments

Polarization and Recovery Experiments

Cells were constructed with the electrolytic manganese dioxide electrodes as cathodes as shown in Fig. 1. The vessels used for most of the cells were of approximately 50 ml volume. A cylindrical anode of silver sheet of a size to fit close to the wall of the vessel surrounded the cathode. Its surface area was much larger than that of the cathode. A silver-silver chloride reference electrode in 1*M* potassium chloride solution (not shown) was connected by a bridge of the cell electrolyte terminating in the bridge receiver shown. The latter ended in a capillary tip at the surface of the manganese dioxide. Several different electrolytes were used, and in some of them other anodes were substituted for the silver sheet in order to prevent objectionable changes in the solution resulting from reactions at the anode. Lead anodes were used for electrolytes containing sulfate, perchlorate, or fluoride ions. When the electrolyte contained zinc chloride a zinc anode was used. For cells

with lead or zinc anodes the vessels were Pyrex beakers of about 180 ml capacity.

When a cell was completed it was placed in an air bath at 25 ± 0.2°C and the open circuit potential difference between the manganese dioxide and reference electrodes measured at intervals until a fairly constant potential was attained. The *p*H of a sample of the electrolyte was then measured by means of a Beckman *p*H meter. A current of 0.8 ma (0.1 ma/cm² of cathode surface) was passed for 15 minutes between the manganese dioxide electrode and the anode, and the potential difference between the manganese dioxide and reference electrodes was measured at timed intervals. At the end of the 15 minute discharge, and immediately after a potential measurement, the circuit was opened and potential measurements were continued until constancy was reattained. A recovery period of at least 24 hours was allowed. The *p*H was measured again after recovery. Usually such discharge and recovery measurements were repeated several times. In Fig. 2 the potential in volts is plotted against time for seven successive discharges and recoveries of a single electrode. These curves are typical of a large number of results, except that the number of discharges was seldom as large as seven.

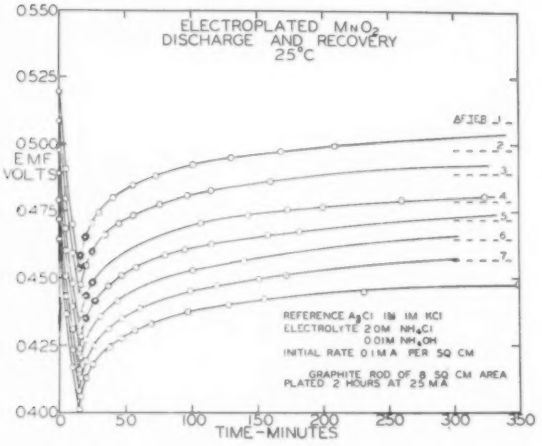

FIG. 2. A series of seven successive 15 minute discharges and recoveries of an electrolytic manganese dioxide electrode.

It was found that the successive discharges could be plotted as a family of curves in which each curve after the first fell just below the preceding one. The constant potential attained after discharge was always lower than the initial potential. In Fig. 2 the constant potentials attained are given by the dotted lines at the right. Each dotted line is at the same value as the initial potential of the next discharge. Each discharge caused a decrease in the equilibrium open-circuit electrode potential.

Another notable feature of the curves is that the recovery curve could be extrapolated back almost exactly to the last point on the discharge portion of the curve. This was true for all electrodes except a few having very thick manganese dioxide coatings. This shows the absence of appreciable *IR* drop in the potential measurement and eliminates resistance changes from consideration in the explanation of the polarization and recovery. It also serves to emphasize the slowness of the recovery process as compared with the recovery of many other electrode systems.

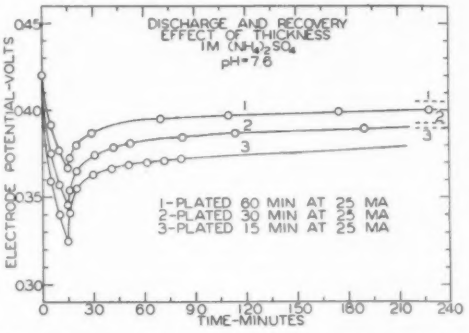

FIG. 3. Effect of thickness of the manganese dioxide on discharge and recovery.

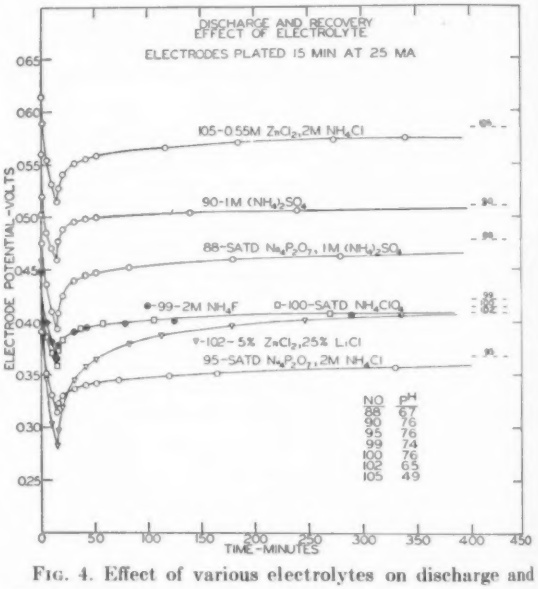

FIG. 4. Effect of various electrolytes on discharge and recovery.

The decrease in open-circuit electrode potential cannot be explained as caused by *p*H changes. The measured *p*H changes were variable, but in buffered electrolytes were seldom more than a few hundredths of a *p*H unit and often practically zero. The calculated *p*H change for a 15 minute discharge is about 0.01 *p*H unit, corresponding to less than a millivolt change in electrode potential.

While the results of the discharge and recovery experiments were all qualitatively similar, there were some quantitative differences worthy of notice. One such difference was in the polarization of electrodes of different thickness, illustrated in Fig. 3. The three electrodes were plated 15, 30, and 60 minutes, respectively, under otherwise constant conditions. The electrolyte was $1M$ ammonium sulfate and $0.01M$ ammonia. Two of the curves were moved in the vertical direction to make the initial points of all three coincide. It is shown that polarization is largest in the thinnest electrode and smallest in the thickest. Similar results were obtained when the electrolyte contained zinc chloride and had a pH of 5.2.

The effect of various electrolytes on the polarization and recovery is shown in Fig. 4. The curves are

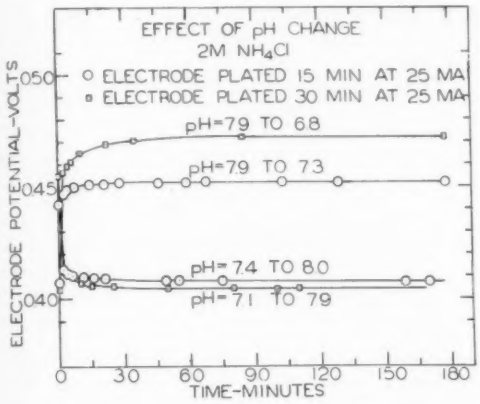

FIG. 5. Response of the open-circuit potential of the electrolytic manganese dioxide electrode to change in pH. The pH of the electrolyte was changed as shown at zero time; the curves give the subsequent change in electrode potential.

much alike for all of the electrolytes containing ammonium ion. All of these were buffered, either by zinc chloride, sodium pyrophosphate, or ammonia. The curve for the lithium chloride electrolyte differs in showing much more polarization and a correspondingly larger recovery. This electrolyte was the least well buffered[3]. Whether or not the difference in buffering accounts for all of the difference in polarzation was not determined, but unbuffered sodium sulfate electrolytes gave similar large polarization.

It is evident that pH changes can cause at least some of the polarization, and it is necessary to ask whether or not they can cause all of it. The slowness of the recovery suggests the presence of another factor. The rate of recovery from the effect of pH changes in the solution was tested by making sudden changes in the pH of an electrolyte and measuring the electrode potential at intervals until constancy was attained. The apparatus was like that described above except that the anode was omitted and two electrolytic manganese dioxide electrodes were included instead of one. The electrolyte was $2M$ ammonium chloride to which either ammonia or hydrochloric acid was added when it was desired to change the pH. The results are shown in Fig. 5. When the pH was changed in either direction the electrode potential rose or fell rapidly to a point not far from the new equilibrium value, then changed more slowly for a period of about 30 minutes and remained constant thereafter. Therefore, pH changes of this type

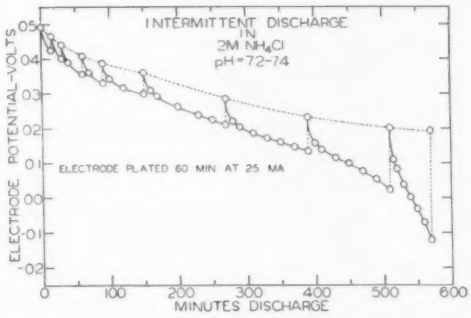

FIG. 6. Intermittent discharges with intervening periods of recovery with an ammonium chloride electrolyte. The dotted curve is an open-circuit discharge curve.

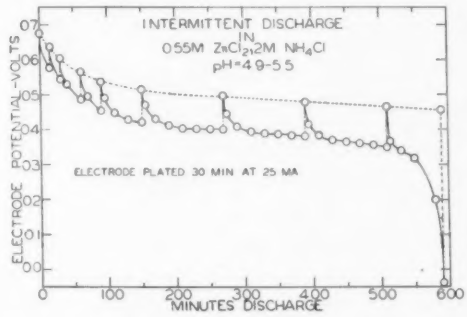

FIG. 7. Intermittent discharges with intervening periods of recovery in the presence of zinc chloride.

cannot account for the slowness of the recovery from polarization.

Discharge Experiments

A number of electrodes were completely discharged by a series of intermittent discharges with periods of recovery from polarization between. Recovery periods of 24 hours were allowed, this time being sufficient for attainment of electrode potentials within a few mv of the equilibrium values. The change of open-circuit electrode potential during a discharge could then be shown by plotting the equilibrium values and connecting by a curve. Such curves are shown as the dotted curves in Fig. 6 and 7 along with the closed circuit curves. The vertical

[3] The authors are indebted to Richard S. Johnson for testing the buffer capacities.

dotted lines represent recovery from polarization, since only discharge time is plotted.

The curves for electrodes with ammonium chloride and ammonium sulfate electrolytes were much alike. The former is shown in Fig. 6. The open-circuit electrode potential decreased throughout the discharge with the most rapid decrease at the beginning and the least at the end. In Fig. 7, with zinc ions present, the curve differed from Fig. 6 in being flatter after the initial curved portion. Pyrophosphate ion gave a discharge curve as in Fig. 7.

The *p*H of the electrolyte was measured throughout each discharge, and the initial and final values are given in the figures. The changes were entirely too small to account for the electrode potential changes.

The curves are best understood if it is assumed that the product of reduction of the manganese dioxide is not formed as a pure solid phase, but rather as a solid solution of the lower oxide in manganese dioxide. The activities of both the higher and lower oxides can then be expected to vary with the progress of the discharge and cause a corresponding variation in the electrode potential. The application of this assumption to the explanation of the recovery from polarization is discussed below.

TABLE I. *Capacity of manganese dioxide electrodes in various electrolytes. Electrodes plated 15 min at 25 ma, theoretical capacity, 167 ma-min*

Electrolyte	*p*H	No. of electrodes	Capacity, per cent of theoretical
NH_4Cl, 2*M*, + NH_3, 0.01*M*	7.30	3	80 ± 17
NH_4Br, 2*M*, + NH_3, 0.01*M*	7.02	2	113 ± 1
NH_4F, 2*M*, + NH_3, 0.01*M*	7.42	4	106 ± 10
$(NH_4)_2SO_4$, 1*M*, + NH_3, 0.01*M*	7.6	3	115 ± 2
NH_4ClO_4, 1*M*, + NH_3, 0.01*M*	7.62	2	110 ± 5
LiCl, 25%, + $ZnCl_2$, 5%	6.62	2	114 ± 1
NH_4Cl, 2*M*, + $ZnCl_2$, 0.55*M*	5.1	2	155 ± 6
NH_4Cl, 2*M*, + $Na_4P_2O_7$, sat'd	7.60	2	140 ± 8
$(NH_4)_2SO_4$, 1*M*, + $Na_4P_2O_7$, sat'd	6.70	2	147 ± 3

The assumption of solid solution formation throws some light on the flatter course of the discharge curve in Fig. 7 and the similar discharge in presence of pyrophosphate compared with that of Fig. 6. Pyrophosphate ion forms a highly colored complex ion with manganese(III) ion, and the color of the solution in the latter part of the discharge of Fig. 7, showed its presence. Removal of trivalent manganese from the electrode system should cause flattening of the discharge curve, since less remains to lower the electrode potential. It must be assumed that, in the early portion of the discharge curve where the activity of the lower oxide is small, little or none has been withdrawn from the electrode system. The effect of zinc ion may be considered to be like that of pyrophosphate since formation of the compound $Zn(MnO_2)_2$, or $ZnO \cdot Mn_2O_3$, is possible (9, 4). The discharge and recovery experiments of Fig. 4 were carried out in the early part of the discharge, and there is little or no effect of zinc or pyrophosphate ion apparent.

A large number of electrodes were discharged by a continuous discharge, or a discharge with only a few interruptions. The effect of an interruption on the results was within the limits of reproducibility. The initial current was 0.1 amp/cm² in all cases. It decreased somewhat during the discharge, but occasional measurements allowed a satisfactory summation of ma-minutes. A theoretical capacity was calculated from the data on the preparation of the electrodes. A valence change of two for manganese was assumed for the plating operation, and a current efficiency of 89 per cent, in view of the analyses of sample electrodes described above. It was also assumed that the valence change on discharge was one, which is somewhat arbitrary (9). Table I gives a summary of the discharge data for electrode plated 15 minutes with a current of 25 ma.

In several ammonium salt solutions and the concentrated lithium chloride the average capacities of from two to four electrodes were in as good agreement with each other as could be expected from the reproducibility, and were in excess of 100 per cent. The latter indicates that the assumption of a trivalent manganese compound as the final product is incorrect, in agreement with Copeland and Griffith (9). Electrolytes containing zinc or pyrophosphate ions gave still larger capacities, corresponding to reduction even beyond the state of trimanganese tetroxide. This is in apparent disagreement with Copeland and Griffith, who obtained no useful discharge from a bobbin made with hetaerolyte, $Zn(MnO_2)_2$. Since manganese oxyhydroxide, MnOOH, gave a discharge under similar conditions they concluded that the formation of hetaerolyte in the dry cell should be prevented, if maximum capacity is desired. However, if hetaerolyte is a secondary instead of a primary product of the cell reaction its formation might not prevent reduction beyond the trivalent stage. If the present experiments can be taken as indicative of what would take place in a dry cell, hetaerolyte formation should not only promote larger capacity, but also a more favorable discharge curve. Pyrophosphate leads to much the same results as zinc ion. The explanation of the largest discharges is incomplete as yet.

The capacities of the electrodes in the ammonium chloride electrolyte were lower than in the other electrolytes. While there was considerable variability among duplicate electrodes, the difference between

the ammonium chloride electrodes and the others is larger than the variability. In similar experiments on thicker electrodes this difference was not apparent, and no explanation can be offered at present.

Discharge curves for some of the electrodes of Table I are shown in Fig. 8. The curves for electrolytes of five different ammonium salts buffered with ammonia are much alike in shape. The curve for the lithium chloride shows the effect of larger polarization in falling below the others for most of its course, though it starts above most of them. The curves for the electrolytes containing zinc and pyrophosphate ions are much more nearly flat after the initial portions, as might be expected from the open-circuit discharge curves.

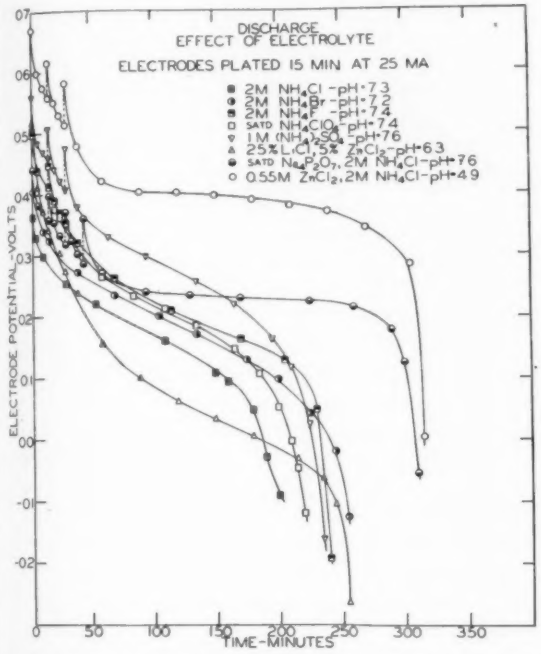

FIG. 8. Effect of the electrolyte on the discharge of the electrolytic manganese dioxide electrode; closed-circuit discharge curves.

Similar discharges were carried out on electrodes plated for 30 and 60 minutes, with general agreement with the results for the 15 minute electrodes. One difference was noticed. From the thicker electrodes some black finely divided material often separated during discharge. This was true only occasionally with the 30 minute electrodes, but always with the 60 minute electrodes. The amount of the black material varied considerably, and the larger it was the smaller the capacity of the electrode.

The capacities of the 60 minute electrodes in ammonium salt solutions gave an average of 73 per cent of theoretical. It is believed that the black material separated from the electrodes was not sufficient to account for all of the difference between this and the average for the 15 minute electrodes. Still thicker electrodes gave an increasingly smaller percentage of the theoretical capacity as the thickness increased. From the discharge data an estimate can be made of the maximum thickness of a manganese dioxide layer (or particle) that can be discharged completely. Some of the 30 minute electrodes gave as high percentages of the theoretical capacity as the 15 minute electrodes, none of the 60 minute electrodes gave as much. Therefore, it was assumed that a 45 minute electrode would have the maximum thickness. Such an electrode should have a layer 7 microns thick. From different data Drotschmann (21) estimated that a particle in a bobbin is usable to a depth of 6 microns. The agreement is doubtless somewhat fortuitous.

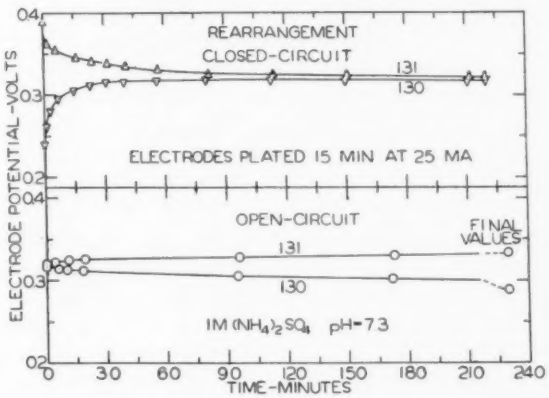

FIG. 9. Upper half: closed-circuit potentials of a partially discharged and an undischarged electrode connected together. Lower half: open-circuit potentials of the same electrodes after having been connected and disconnected.

Rearrangement

If solid solutions are formed between manganese dioxide and lower oxides, it follows that a difference of potential must exist between electrodes of different solid solution composition, or between regions of different composition in the same electrode system. When an electrode system is discharged unequally, as in the discharge of a bobbin (11, 12), a difference of potential must exist on opening the circuit between the parts unequally discharged. Since the two parts are connected by a conductor and are in contact with solution, they constitute a cell with closed circuit. Flow of current should then tend to correct the inequality and bring the manganese oxides to uniform composition. It has been convenient to call this process a rearrangement.

A rearrangement process was carried out experimentally. A cell like those used for discharge ex-

periments was constructed, but with two manganese dioxide electrodes similar to those of Table I, and with an ammonium sulfate electrolyte. When approximate constancy of electrode potential had been attained, one of the electrodes was discharged by approximately half its capacity and allowed to recover from polarization. There was then a difference of 0.15 volt in electrode potential between the two. They were connected through a milliameter and variable resistance and an initial current of 0.1 ma/cm^2 was allowed to pass. The current decreased fairly rapidly and eventually became practically constant at 5 μa/cm^2. The changes in closed circuit electrode potential are shown in the upper part of Fig. 9. When approximate constancy was attained the circuit was opened and the open-circuit potentials measured for some time, giving the values shown in the lower part of Fig. 9. Evidently the time allowed was insufficient for complete rearrangement. The interpretation of the results was checked by separate complete discharge of the two electrodes. The observed capacities when corrected for the quantity of electricity that had passed from one electrode to the other agreed with what was expected on the basis of the previous discharge experience recorded in Table I.

If a manganese dioxide particle is discharged unequally in different portions, a somewhat similar situation exists, but without the advantage of the good electrical connection through an external circuit. In this case rearrangement by diffusion is possible.

Discussion

A theory of the discharge and recovery processes in electrolytic manganese dioxide electrodes can be formulated on the basis of the experiments described above. It is assumed that, when the electrolytic electrode is discharged, reduction of manganese dioxide takes place next to the graphite surface rather than at the exterior surface. Evidence for this is that during the discharge of the thicker electrodes some of the material separates from the electrode, doubtless from the exterior, and such separation is always associated with loss of capacity. This loss of capacity indicates that the separated material is dioxide rather than lower oxide.

Next, it is assumed that the electrode potential varies with the composition of the oxide in contact with the electrode. This involves also the assumption that solid solutions are formed between the lower oxide and the dioxide, and that the oxidation potential is dependent on the composition of the solid solution. In support of this assumption Johnson (23) found that electrodes made with mixtures of precipitated manganese dioxide and manganese oxyhydroxide have potentials varying linearly with the logarithm of the ratio of the two oxides. An important part of the polarization results from the formation of a layer of oxide relatively rich in the lower oxide at the graphite surface.

It must be assumed next that lower oxide in contact with manganese dioxide can diffuse into the dioxide to form the solid solution, or the dioxide can diffuse into the lower oxide, or both. This assumption has been made by Coleman (11). This diffusion must be much slower then the equivalent diffusion in a liquid solution. Its mechanism, as explained above, might be merely the movement of electrons and protons. The discharge curves (left-hand branches of Fig. 2, 3, and 4) are not straight lines; their slopes decrease with time. This is explained as the result of the diffusion, the rate increasing as the lower oxide accumulates. When the discharge is continued long enough, a state is reached in which diffusion balances reduction, as in some of the longer discharges shown in Fig. 6 and 7. The accumulation of excess lower oxide at the graphite surface can be considered concentration polarization in which the concentration of a solid solution is involved.

During the discharge the diffusion is more rapid in a thick layer of manganese dioxide than in a thin one, as shown by the greater curvature of the discharge curves for the thick electrodes in Fig. 3. Lower oxide diffusing into a thick layer produces a solid solution of smaller concentration than the same amount diffusing into a thin layer. Consequently, for a time, the concentration gradient is larger for the thick layer, and the rate of diffusion faster.

When the discharge is discontinued, the formation of the lower oxide stops, but its removal from the graphite surface and replacement by dioxide continues. This is the recovery process, and its rate decreases with time as the concentration gradient in the solid decreases.

The decrease in open circuit electrode potential with discharge can be explained as the result of the decrease in manganese dioxide activity as the dioxide is diluted with lower oxide, and the increase in the lower oxide activity as its concentration in the solid increases. It follows that the open-circuit electrode potential should decrease less when the manganese dioxide is thick than when it is thin for the same amount of discharge. This was found to be true.

Zinc and pyrophosphate ions do not appreciably affect the discharge and recovery experiments shown in Fig. 4, but have an effect on the complete discharge as shown in Fig. 8. In the latter the effect is noticeable only after the initial rapid decrease in electrode potential. The discharge and recovery experiments (Fig. 4) were carried out in the early portion of the discharge curve. Zinc and pyrophosphate

ions affect the discharge by removal of the lower oxide and they cannot do this effectively in the early part of the discharge where the lower oxide activity is small.

The equation of Hackett and Feely (24) for the recovery process does not fit the data of this investigation. However, if the open circuit electrode potential is plotted against the logarithm of the time counted from the instant of the opening of the circuit after polarization, the points fall very satisfactorily on a straight line. This relationship is too simple to account for the condition of zero time and for the constancy attained after long time.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the JOURNAL.

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